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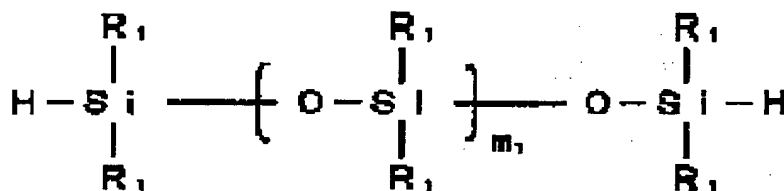
**(54) GEL ELECTROLYTE
FOR LITHIUM SECONDARY
BATTERY**

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain a gel electrolyte having an improved electric conductivity by alternately copolymerizing a polysiloxane compound having SiH bond at both molecular terminals and polyalkylene oxide compound.

SOLUTION: A polysiloxane compound compound of formula I and a polyalkylene side compound of formula II are used. When a crosslinked structure is desired, compounds of formula I, II, and III are used or a polysiloxane having at least three SiH groups and compounds of formula II, III, and IV are used. In the formulas, R1 is a

hydrocarbon group containing no aliphatic unsaturation; m_1 is 0-500; R_{21} and R_{22} are each a hydrocarbon group having a terminal double bond; a is 2-4; n_{21} and n_{22} are each an integer of 1 or higher; R_{23} is H, a saturated hydrocarbon group, or acyl; R_{31} is H or alkyl; R_{32} is an organic group or a direct bond; b is 2-4; l_3 is an integer of 2 or higher; and Z_{31} is a substituent containing C on N. Monomeric or oligomeric ray materials are copolymerized by hydrosilylation to obtain the objective electrolyte.



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(71) 出願人 000005980

三菱製紙株式会社

東京都千代田区丸の内3丁目4番2号

(71) 出願人 000230331

日本ユニカー株式会社

東京都千代田区大手町2丁目6番1号

(72) 発明者 高岡 和千代

東京都千代田区丸の内3丁目4番2号 三

菱製紙株式会社内

(74) 代理人 100106596

弁理士 河備 健二

最終頁に続く

(54) 【発明の名称】 リチウム2次電池用ゲル状電解質

(57) 【要約】

【課題】 リチウム2次電池に適した新規なゲル状電解質の提供。

【解決手段】 両末端にSi-H基を有する特定のポリシロキサン化合物と特定のポリアルキレンオキサイド化合物を交互に重合して得られる高分子化合物、これらポリシロキサン化合物とポリアルキレンオキサイド化合物にさらに特定の多官能性化合物を反応させて得られる架橋構造体、又は三つ以上のSi-H基を有するポリシロキサン化合物と特定のポリアルキレンオキサイド化合物にさらに特定の多官能性化合物を反応させて得られる架橋構造体、或いはさらにはこれら高分子化合物や架橋構造体に特定の変性シリコーンを組み合わせたものを、少なくとも含有することを特徴とするリチウム2次電池用ゲル状電解質により提供。

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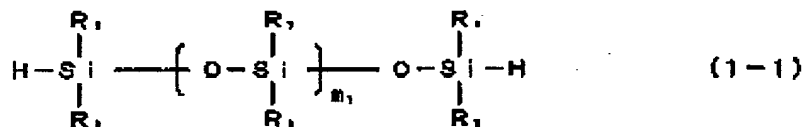
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【特許請求の範囲】

* させて得られる高分子化合物を、少なく
とを特徴とするリチウム2次電池用ゲル
【化1】

【請求項1】 両末端にSi-H基を有する下記的一般
式(1-1)のポリシロキサン化合物と、一般式(2-
1)のポリアルキレンオキサイド化合物とを交互に重合*



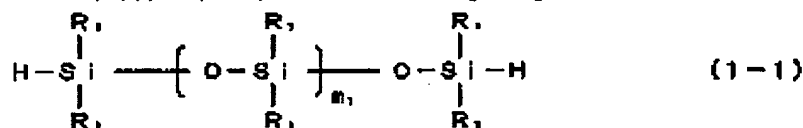
(式中、 R_1 は互いに独立して脂肪族不飽和を含まない
一価の炭化水素基を示し、 n_1 は0から500までの整※10 【化2】



(式中、 $\text{R}_{2,1}$ は末端二重結合を有する一価の炭化水素
基を示し、 a は2から4の整数を示し、 $n_{2,1}$ は1以上
の整数を示す。)

★ 1) のポリアルキレンオキサイド化合物
- 1) の多官能性化合物とを反応させて、
造体を、少なくとも含有することを特徴
2次電池用ゲル状電解質。

【請求項2】 両末端にSi-H基を有する下記的一般
式(1-1)のポリシロキサン化合物と、一般式(2-★



(式中、 R_1 は互いに独立して脂肪族不飽和を含まない
一価の炭化水素基を示し、 n_1 は0から500までの整☆ 【化4】



(式中、 $\text{R}_{2,1}$ は末端二重結合を有する一価の炭化水素
基を示し、 a は2から4の整数を示し、 $n_{2,1}$ は1以上◆
◆の整数を示す。)



(式中、 $\text{R}_{3,1}$ は水素原子或いはアルキル基を示し、 $\text{R}_{3,2}$
は二価の有機基又は直接接合を示す。 l_3 は2以上
の整数であり、 $\text{Z}_{3,1}$ は炭素または窒素を含む置換基で
あって l_3 と同じ数の価数を持つ基である。)

* リアルキレンオキサイド化合物と、一般
30 多官能性化合物とを反応させて得られる
少なくとも含有することを特徴とするリ
用ゲル状電解質。

【請求項3】 三つ以上のSi-H基を有するポリシロ
キサンと、下記的一般式(2-1)又は(2-2)のボ*



(式中、 $\text{R}_{2,1}$ は末端二重結合を有する一価の炭化水素
基を示し、 a は2から4の整数を示し、 $n_{2,1}$ は1以上※
※の整数を示す。)



(式中、 $\text{R}_{2,2}$ は末端二重結合を有する一価の炭化水素
基を示し、 $\text{R}_{2,2}$ は水素原子、一価の飽和炭化水素基ま
★ $_{2,2}$ は1以上の整数を示す。)

40 【化8】

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【請求項6】 請求項3に記載の架橋構造体と、40℃における粘度が10000cP以下である変性シリコンとを、少なくとも含有することを特徴とするリチウム2次電池用ゲル状電解質。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】この発明は、新規なリチウム2次電池用ゲル状電解質、さらに詳しくは電気伝導性に優れた新規なリチウム2次電池用ゲル状電解質に関する。

【0002】

【従来の技術】リチウム2次電池は、理論エネルギー密度が高く、ポータブル電子機器電源を始め、電気自動車、電力貯蔵用電源等その応用範囲が広い。従来のリチウム2次電池に用いられている電解質は、リチウムの高い反応性のためにイオン伝導度の高い水溶液系が使えないことから、リチウム塩を非水溶液中に溶解させた有機電解液が用いられていた。しかし有機電解質では、液状であるため、電池が破損したり、過充電時の発熱などにより気化し、常に爆発の危険が伴い、そのために十分な安全策を講じる必要があり、それがまた電池のコストを上昇させる原因や使い勝手の悪さになっていた。

【0003】これに対し、最近では高分子電解質やゲル電解質などが提案されている。これらは、比較的高いイオン伝導性、広い電位窓、良好な薄膜形成性、柔軟性、軽量性、弾性、透明性等を備えた優れた特徴を持っている。2次電池では、多くの電極活物質が作動中のその体積を変化させているので、高分子電解質の柔軟性や弾性的特性は特に重要である。また、電極材料の脱離による、繰り返し使用時における電池容量の低下や、正負極材料の短絡防止能もあると言われている。

【0004】このような高分子電解質として、Advanced Materials, 10, 439 (1998) では、多種の電解質が提案されている。ここでは、ポリエチレンオキサイドや、ポリエチレンオキサイドとポリシランとの複合物、ポリエチレンオキサイドとポリフォスファゼンとの複合物や、ポリエチレンオキサイドを構造単位に持ちエポキシ基やイソシアネート基、更にはシロキサン構造を有する架橋構造のポリマーなどが紹介されている。特にポリシロキサン構造との複合物は、

*質である。

【0005】ポリシロキサンを構造単位分子電解質は、ポリエチレンオキサイド化合物として、J. Polym. Sci. m. Lett. Ed., 22, 659 Solid State Ionics, (1985), 特開昭63-13640平8-21389号公報、特開昭8-7などに記載されているが、化合物自身のみであったり、電極材料の脱離を抑え、薄層架橋構造体を得られなかったり、十分な得られないことなどが問題となり、未だにない。

【0006】

【発明が解決しようとする課題】本発明のポリシロキサンを構造単位として有するものも問題点を解消し、リチウム2次電池なゲル状電解質を提供することにある。

【0007】

【課題を解決するための手段】本発明者を解決すべく鋭意検討を重ねた結果、両基を有する特定のポリシロキサン化合物ルキレンオキサイド化合物を交互に重合分子化合物や、これらポリシロキサン化合物ルキレンオキサイド化合物にさらに特定のH基を有するポリシロキサン化合物と特定の多反応させて得られる架橋構造体や、さらに子化合物や架橋構造体に特定の変性シリ

【0009】

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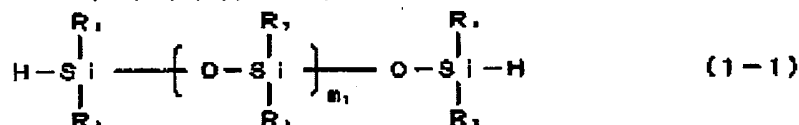
の整数を示す。)

【0011】また、本発明によれば、両末端にSi-H基を有する下記的一般式(1-1)のポリシロキサン化合物と、一般式(2-1)のポリアルキレンオキサイド化合物と、一般式(3-1)の多官能性化合物とを反応*

*させて得られる架橋構造体を、少なくとも特徴とするリチウム2次電池用ゲル状物。

【0012】

【化11】



(式中、 R_1 は互いに独立して脂肪族不飽和を含まない一価の炭化水素基を示し、 m_1 は0から500までの整数を示す。)

10※【0013】

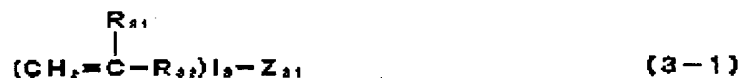
【化12】



(式中、 $R_{2,1}$ は末端二重結合を有する一価の炭化水素基を示し、 a は2から4の整数を示し、 $n_{2,1}$ は1以上の整数を示す。)

★【0014】

【化13】



(式中、 $R_{3,1}$ は水素原子或いはアルキル基を示し、 $R_{3,2}$ は二価の有機基又は直接接合を示す。 l_3 は2以上の整数であり、 $Z_{3,1}$ は炭素または窒素を含む置換基であって l_3 と同じ数の価数を持つ基である。)

20☆1)又は(2-2)のポリアルキレンオと、一般式(3-1)の多官能性化合物得られる架橋構造体を、少なくとも含有とするリチウム2次電池用ゲル状電解質。

【0015】さらに、本発明によれば、三つ以上のSi-H基を有するポリシロキサンと、下記的一般式(2-☆

【0016】

【化14】



(式中、 $R_{2,1}$ は末端二重結合を有する一価の炭化水素基を示し、 a は2から4の整数を示し、 $n_{2,1}$ は1以上の整数を示す。)

◆【0017】

【化15】



(式中、 $R_{2,2}$ は末端二重結合を有する一価の炭化水素基を示し、 $R_{2,3}$ は水素原子、一価の飽和炭化水素基またはアシル基を示し、 b は2から4の整数を示し、 n *

* $n_{2,2}$ は1以上の整数を示す。)

【0018】

【化16】



(式中、 $R_{3,1}$ は水素原子或いはアルキル基を示し、 $R_{3,2}$ は二価の有機基又は直接接合を示す。 l_3 は2以上の整数であり、 $Z_{3,1}$ は炭素または窒素を含む置換基であって l_3 と同じ数の価数を持つ基である。)

もなり得る。そしてこれらの物質は、同いはオリゴマーの状態にある原料をヒドによって重合させて作製される。ヒドロ

40 は アリル、ビニル等のアルケニル基を

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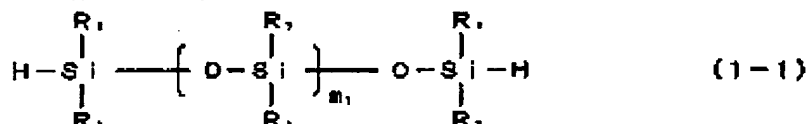
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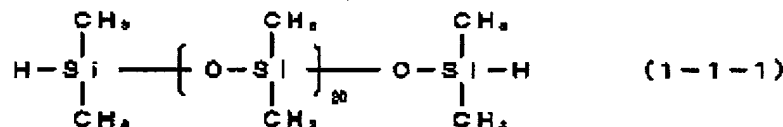
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白金-ビニルシロキサン錯体、白金-フォスフィン錯体、白金-フォスファイト錯体、白金アルコール触媒等が挙げられる。ヒドロシリル化反応の際、白金触媒は、通常0.0001重量%から0.1重量%程度添加される。また、この反応は、反応速度の温度依存性が大きいことから、加熱をして反応を促進させることができる。これは、ヒドロシリル化反応の大きな利点であって、反応物を適度な粘性で混合し、成形した後加熱すれば、一気に所望の形状のゲル状物が得られる。また、この時、水などのほかの副生成物や、反応直後の体積変動がほとんどなく、電池用のゲル化方法としては優れた手法である。

【0021】本発明の一つ態様としては、ヒドロシリル*



式中、 R_1 は互いに独立して脂肪族不飽和を含まない一価の炭化水素基を示す。 m_1 は0から500までの整数であって、好ましくは2から100までの整数、更に好ましくは5から30程度の整数である。かかるポリシロキサン化合物としては、具体的には、 R_1 がメチル基、※



【0024】次に、エチレングリコールなどのジアルコール体にエチレンオキサイド等をエポキシ基の開環反応にて連鎖重合させると、両末端に水酸基を有するポリアルキレングリコールが得られる。例えば、このように得られたポリアルキレングリコールの両末端の水酸基をビニルオキシ基、アリルオキシ基、或いは2-メチルアリルオキシ基等に置換し、両末端にアルキレン基を有する次の一般式(2-1)で示されるポリアルキレンオキサ★



式中、 R_2 は末端二重結合を有する一価の炭化水素基を示し、 a は2から4の整数を示し、 n_2 は1以上の整数を示す。この場合、 R_2 の具体例としては、 $CH_2=CHCH_2-$ 、 $CH_2=CHCH_2CH_2-$ 、 $CH_2=CH-$ 、 $CH_2=C(CH_3)CH_2-$ 、 $CH_2=C(CH_3)-$

* 化反応を利用して、ポリシロキサン構造にオキサイド構造が交互に入り込み、高物得られる。このような構造物の合成例えば、まず、ジメチルジクロロシランの加水分解や、ジメトキシジメトキシシメチルシランの加水分解により-H基を有する次の一般式(1-1)シロキサン化合物を得る。この時、 Si 単量体の仕込量を変えることによって、化合物の分子量を変えることができる。

【0022】

【化17】

※ m_1 が20である、次の式(1-1-1)化合物がある。

【0023】

【化18】

★ イド化合物を得る。この際、ポリエチレンようにオキシエチレンユニット単独でも、エチレン基、メチルオキシエチレン基、エチレン基などのユニットを、ランダム或いは重合し、これをポリアルキレンオキサで用いることもできる。

【0025】

【化19】

(2-1)

☆ である。また、 n_2 の好ましい範囲は20程度である。かかるポリアルキレン化合物としては、具体的には、式(2-1)る化合物がある。

【0026】

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にアルケニル基が残り、逆にポリシロキサン化合物が過剰であれば、両末端にSi-H基が残存する。そして、得られる目的化合物(1)の平均分子量は、反応物の仕込み濃度などに依存する。

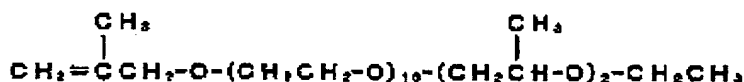
【0028】また、ポリアルキレンオキサイド部の片末端をアルコキシ変性したもの(後述の一般式(2-2)で示される化合物)を加えると、これが最終重合端となり、これによってその平均分子量をコントロールできる。このようにして得られた目的化合物(1)は、ポリシロキサン構造とポリアルキレンオキサイド構造を交互に持ち、その繰り返し構造数は、2から100程度、好ましくは4から80程度である。かかるポリアルキレンオキサイド部の片末端をアルコキシ変性した化合物の製*



(2-2)

式中、 R_{22} は末端二重結合を有する炭化水素基を示し、 R_{23} は水素原子、一価の飽和炭化水素基またはアシル基を示し、 b は2から4の整数を示し、 n_{22} は1以上の整数を示す。この場合、 R_{22} の具体例としては、 $CH_2=CHCH_2-$ 、 $CH_2=CHCH_2CH_2-$ 、 $CH_2=CH-$ 、 $CH_2=C(CH_3)CH_2-$ 、 $CH_2=CHCH_2H_4-$ 等があり、好ましくは $CH_2=CHCH_2-$ や $CH_2=C(CH_3)CH_2-$ である。 n_{22} の好ましい範囲としては、4から20程度である。*

(2-2-1)



【0031】次に、本発明の別の態様としては、両末端にSi-H基を有する一般式(1-1)のポリシロキサン化合物に、両末端にアルキレン基を有する一般式(2-1)のポリアルキレンオキサイド化合物と、架橋構造を形成するための多官能性化合物(後述の一般式(3-1)で示される多官能性化合物)を混合し、ヒドロシリル化反応によって得られる架橋構造体は、本発明の目的化合物(2)である。この時、式(1-1)の化合物、式(2-1)の化合物、及び式(3-1)の化合物は、式(1-1)の化合物のSi-H基を1とすると、式

*造方法としては、例えば、メタノール、タノールなどのアルコールにエチレンオボキシ基を有する化合物を、開環重合にて、一方の末端に水酸基を有するポリアルキレンオキサイドを得る。このように得られた次の一で示される化合物は、ポリアルキレンオの末端にある水酸基をビニルオキシ基、基、或いは2-メチルアリルオキシ基等にアルケニル基を有し、片末端がアルコポリアルキレンオキサイド化合物である。

【0029】

【化21】

※ R_{23} における一価の飽和炭化水素基のチル基、エチル基等の炭素数1から18が挙げられる。 R_{23} の好ましい例として、メチル基、エチル基、ブチル基、まある。かかる片末端がアルコキシ変性ポリアルキレンオキサイド化合物としては、具体的(2-2-1)で示される化合物がある。

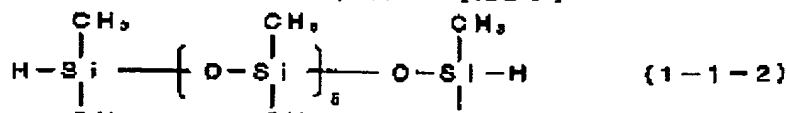
【0030】

【化22】

★(2-1)の化合物のアルケニル基が0.9程度、式(3-1)の化合物のアルケニル基が1.9程度となる比率で反応させ(2)を作製する場合、式(1-1)の化合物としては、 m_1 が好ましくは0か数、更に好ましくは1から20以下の整数望ましい。これに該当する化合物としては、次の式(1-1-2)で示される化

【0032】

【化23】



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基である。R₂は二価有機基又は直接結合を示し、二価の有機基の例としては、メチレン基、エチレン基、フェニレン基等がある。1₂は2以上の整数であり、好ましくは3または4である。Z₂は炭素または窒素を含む置換基であり、1₂と同じ価数を持つ基である。この多官能性化合物に該当するものとしては、具体的には、以下に示す式(3-1-1)、式(3-1-2)、式(3-1-3)、式(3-1-4)、式(3-1-5)、式(3-1-6)、式(3-1-7)、式(3-1-8)、式(3-1-9)、式(3-1-10)、式*10(3-1-2)

* (3-1-11)、或いは式(3-1-等がある。

[0035]

[化25]

(3-1-1)

(CH₂=CHCH₂-O-CH₂),OCH₂

[0036]

[化26]

(CH₂=CHCH₂-O-CH₂),-OCH₂O-CH₂CH=CH₂

[0037]

※ ※ [化27]

(3-1-3)

(CH₂=CHCH₂-O-CH₂CH₂O-CH₂),-OCH₂CH₂

[0038]

★ ★ [化28]

(3-1-4)

$$(\text{CH}_2=\text{CHCH}_2\text{OCH}_2)_2\text{OCH}_2\text{OCH}_2\text{C}(\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2)_2$$

[0039]

☆ [0040]

[化29]

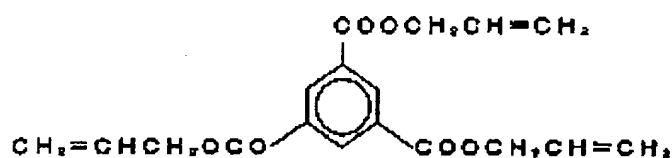
[化30]

(3-1-5)

$$(\text{CH}_2=\text{C}(\text{CH}_3)\text{OCH}_2\text{CH}_2\text{O})_2\text{PO}$$

☆

(3-1-6)

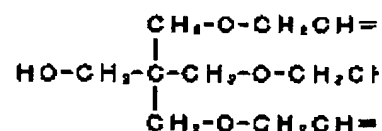
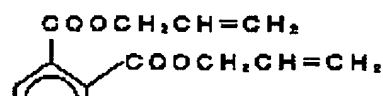


(3-1-8)

[0041]

[化31]

(3-1-7)

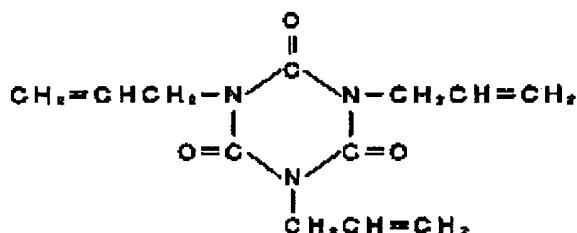


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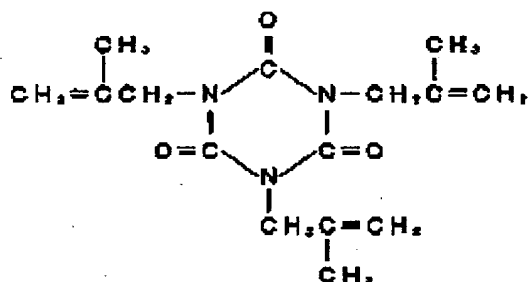
(3-1-10)



【0045】

【化35】

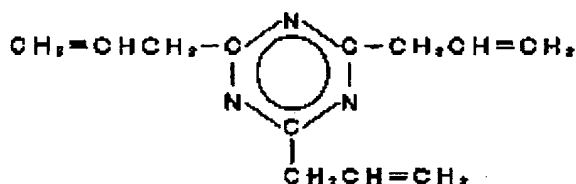
(3-1-11)



【0046】

【化36】

(3-1-12)



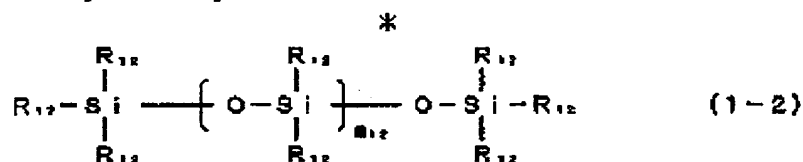
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*【0047】目的化合物(2)を得る場合、(1)のポリシロキサン化合物、一般式リアルキレンオキサイド化合物、更には(1)の多官能性化合物は、分子量の関係、化合物間の相溶性が著しく悪くなる場合は、予め一般式(1-1)の化合物の過剰式(2-1)の化合物をヒドロシル化して、適度の分子量を持つ前駆体を用いて一般式(3-1)の多官能性化合物を作

- 10 構造体を得ることもできる。具体的には、(1)の化合物のSi-H基を1とすると、(1)の化合物のアルケニル基を0.1かになる比率で反応させて前駆体を作製し、(3-1)の多官能性化合物のアルケニル基から1.9程度になる比率で反応させて、
- 20 【0048】次に、本発明のさらに別の三つ以上のSi-H基を有するポリシロキサン式(2-1)又は式(2-2)のポリアルキド化合物と、一般式(3-1)の多官
- 反応して得られる架橋構造体は、本発明(3)である。三つ以上のSi-H基をキサンとしては、下記に示す一般式(1)の直鎖状ポリシロキサン、一般式(1-環状ポリシロキサン、或いは一般式(1)のラダー状ポリシロキサンなどがある。

【0049】

【化37】



式中、R_{1,2}は互いに独立して脂肪族不飽和を含まない一価の炭化水素基または水素原子を示すが、分子中のR_{1,2}の3つ以上は水素原子であり、50個以下が好ましく、更に好ましくは3から10程度である。m_{1,2}は0から500の整数を示す。m_{1,2}の好ましい範囲は2か※

(1-2-1)

※ら100程度であって、更に好ましくはである。なお、これに該当する化合物とには、次の式(1-2-1)の化合物が、

【0050】

【化38】



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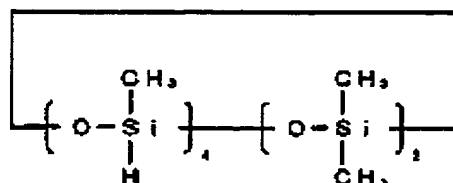
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式中、 R_{13} は水素原子または互いに独立して脂肪族不飽和を含まない一価の炭化水素基を示し、分子中の R_{13} の3から8個は水素原子である。 m_{13} は3から8の整数を示す。なお、これに該当する化合物としては、*

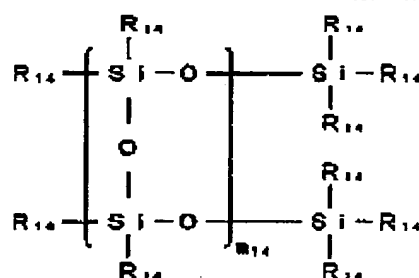
* 具体的には、次の式(1-3-1)の化合物
【0052】
【化40】



(1-3-1)

【0053】

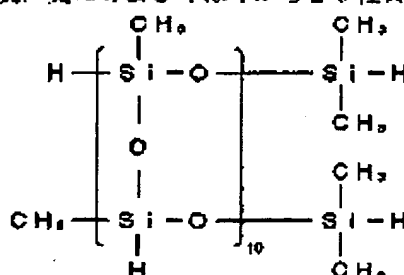
※ ※ 【化41】



(1-4)

式中、 R_{14} は水素原子または互いに独立して脂肪族不飽和を含まない一価の炭化水素基を示し、分子中の R_{14} の3つ以上は水素原子であり、好ましくは50個以下である。 m_{14} は1から50までの整数であって、好ましくは2から30程度、更に好ましくは4から20程度★

★度である。なお、これに該当する化合物としては、次の式(1-4-1)の化合物
【0054】
【化42】



(1-4-1)

【0055】本発明の目的化合物(3)は、このような3つ以上の $\text{Si}-\text{H}$ 基を有するポリシロキサン(2)の $\text{Si}-\text{H}$ 基を1とすると、一般式(2-1)の化合物のアルケニル基が0.1から0.99程度になる比率、或いは一般式(2-2)の化合物のアルケニル基が0.1から0.9程度となる比率で、更に一般式(3-1)の化合物のアルケニル基が0.01から0.8程度となる比率で反応させることによって得られる。また、別の方法としては、目的化合物(2)を得る時と同様に、予め3つ以上の $\text{Si}-\text{H}$ 基を有するポリシロキサンと、一般式

テル変性シリコンやポリエステル変性を意味する。これらの粘性は、40℃以下であるが、好ましくは2000cP以下である。目的化合物(3)のいずれかと、これら変性シリコンの場合には、その比率として、目的化合物と、変性シリコンが0.01から10好ましくは0.1から10重量比程度でされる。

【0057】用いられる変性シリコン

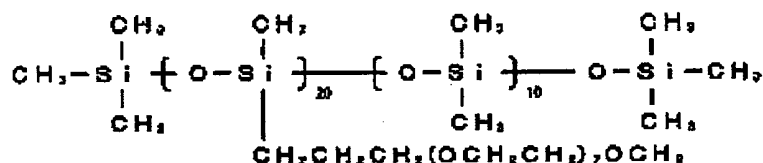
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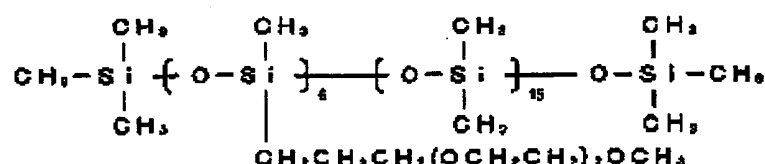
(4-1)



【0059】

* * 【化4.4】

(4-2)



【0060】本発明は、リチウム2次電池の電解質に関するものである。前述した高分子量構造体或いは架橋構造体と、リチウム2次電池が良好に作動するための各種周知の任意材料を組合せた上で使用する。まず、電解質として作動するには、支持電解質が必要である。支持電解質としては、 LiClO_4 、 LiBF_4 、 LiAsF_6 、 LiCF_3SO_3 、 $\text{Li}(\text{CF}_3\text{SO}_2)$ 、 $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ 、 $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$ 、 LiBPh_4 （ここでPhはフェニル基を示す）等のリチウム塩が使用できる。また、リチウム塩を溶解させるための溶剤も使用できる。使用できる溶剤としては、プロピレンカーボネイト、エチレンカーボネイト、γ-ブチロラクトン、ジメチルカーボネイト、ジエチルカーボネイト等のカルボニル結合を有するエステル系化合物、テトラヒドロフラン、1,2-ジメトキシエタン、1,2-エトキシエタン、1,3-ジオキサン等のエーテル系化合物等を単独で或いは混合して使用することができる。さらに、テトラエチレングリコールジメチルエーテル、テトラプロピレングリコールジメチルエーテル等のポリアルキレンオキサイド化合物、ポリアルキレンオキサイドを側鎖に有する変性ポリジメチルシロキサン、ポリアルキレンオキサイドを構造単位に持つ変性ポリアクリレート、ポリアクリロニトリル、ポリフッ化ビニリデン、ポリアルキレンオキサイドを構造単位に持つ変性ポリフォスファゼン等のイオン導電性ポリマーも混合できる。

【0061】リチウム2次電池用の高分子電解質或いはゲル電解質として使用するためには、正負電極材料間

としては、湿式あるいは乾式のいずれも、その目付量は、 100 g/m^2 以下、 $5\sim 50\text{ g/m}^2$ である。使用される有機ポリエステル、ポリプロピレン、ポリエー（登録商標）などであるが、特にこれ訳ではない。多孔質フィルムとしては、ポリチレン、ポリプロピレン等のフィルムを、孔質化したフィルムなどが用いられる。 5 g/m^2 から 30 g/m^2 程度のもの。

【0062】リチウム2次電池に用いられるのは、 LiCoO_2 、 LiNiO_2 、スピネル V_2O_5 、 $\beta\text{-Li}_2\text{MnO}_3$ の混合物、スピネル超格子 Mn_3O_4 、2,5-ジメルカプトジアゾール等の有機ジスルフィド化合物、質として、これを粉末状にして、アセチ

【0063】負極材料とは、金属リチウム、アルミニウム合金、 Li-Pb-Cd 、リチウム-黒鉛化合物、リチウム-難黒鉛リチウム-非晶質錫複合酸化物、非晶質化リチウムなどの負極活性物質を、金属の板などにメッキして、他の場合は正極材料に、アセチレンブラックなどの導電

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プロピレンカーボネイト 100重量部
過塩素酸リチウム 36重量部
0.3%白金触媒 2.5重量部
これを目付量 15 g/m^2 で厚み $30\text{ }\mu\text{m}$ の不織布に含
浸し、 90°C で1時間加熱して、厚み $32\text{ }\mu\text{m}$ のゲル状
電解質(1)を得た。このゲル状電解質(1)の貯蔵弾
性率は、 $8.5 \times 10^3\text{ Pa}$ 、電気伝導性は、 $6.5 \times$
 10^{-4} S/cm であった。一方、市販のリチウム2次*

式(1-1-2)の化合物	67.3重量部
式(2-1-1)の化合物	84.1重量部
式(3-1-1)の化合物	13.7重量部
エチレンカーボネイト	40重量部
プロピレンカーボネイト	60重量部
トリフルオロメタンスルホン酸リチウム	39.8重量部
0.3%白金触媒	1.2重量部

これを目付量 15 g/m^2 で厚み $30\text{ }\mu\text{m}$ の不織布に含
浸し、 90°C で1時間加熱して、厚み $32\text{ }\mu\text{m}$ のゲル状
電解質(2)を得た。このゲル状電解質(2)の貯蔵弾
性率は、 $0.9 \times 10^5\text{ Pa}$ 、電気伝導性は、 $8.0 \times$
 10^{-4} S/cm であった。一方、市販のリチウム2次
電池より正極層と負極層を取り出し、金属アルミニウ
ム、正極層、ゲル状電解質(2)、負極層、及び金属銅※

式(1-1-2)の化合物	67.3重量部
式(2-1-1)の化合物	84.1重量部
0.3%白金触媒	1.4重量部

次ぎに、上記前駆体(3)と次の各化合物を混合した。

前駆体(3)	151.4重量部
式(3-1-1)の化合物	13.7重量部
エチレンカーボネイト	40重量部
プロピレンカーボネイト	60重量部
トリフルオロメタンスルホン酸リチウム	39.8重量部
0.3%白金触媒	1.2重量部

これを目付量 15 g/m^2 で厚み $30\text{ }\mu\text{m}$ の不織布に含
浸し、 90°C で1時間加熱して、厚み $32\text{ }\mu\text{m}$ のゲル状
電解質(3)を得た。このゲル状電解質(3)の貯蔵弾
性率は、 $1.5 \times 10^5\text{ Pa}$ 、電気伝導性は、 $7.5 \times$
 10^{-4} S/cm であった。一方、市販のリチウム2次
電池より正極層と負極層を取り出し、金属アルミニウ
ム、正極層、ゲル状電解質(3)、負極層、及び金属銅★

式(1-2-1)の化合物	43.5重量部
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*電池より正極層と負極層を取り出し、金
ム、正極層、ゲル状電解質(1)、負極
を積層して、リチウム2次電池を作製し
0.1mAの電流値で充放電を行ったと
は、 1.8 mAh/cm^2 であった。

【0066】実施例2

次の各材料を混合した。

式(1-1-2)の化合物	67.3重量部
式(2-1-1)の化合物	84.1重量部
式(3-1-1)の化合物	13.7重量部
エチレンカーボネイト	40重量部
プロピレンカーボネイト	60重量部
トリフルオロメタンスルホン酸リチウム	39.8重量部
0.3%白金触媒	1.2重量部

※を積層して、リチウム2次電池を作製し
0.1mAの電流値で充放電を行ったと
は、 1.8 mAh/cm^2 であった。

【0067】実施例3

20 次の各材料を混合し、 100°C に30分
(3)を作製した。

式(1-1-2)の化合物	67.3重量部
式(2-1-1)の化合物	84.1重量部
0.3%白金触媒	1.4重量部

前駆体(3)	151.4重量部
式(3-1-1)の化合物	13.7重量部
エチレンカーボネイト	40重量部
プロピレンカーボネイト	60重量部
トリフルオロメタンスルホン酸リチウム	39.8重量部
0.3%白金触媒	1.2重量部

★を積層して、リチウム2次電池を作製し
0.1mAの電流値で充放電を行ったと
は、 1.9 mAh/cm^2 であった。

【0068】実施例4

次の各材料を混合し、 100°C に30分
(4)を作製した。

式(1-2-1)の化合物	43.5重量部
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ム、正極層、ゲル状電解質(4)、負極層、及び金属銅を積層して、リチウム2次電池を作製した。この電池を0.1mAの電流値で充放電を行ったところ、その容量*

*は、2.0mAh/cm²であった。

【0069】実施例5

次の各材料を混合した。

式(1-1-1)の化合物	160	重量部
式(2-1-1)の化合物	97	重量部
式(4-1)の化合物	100	重量部
トリフルオロメタンスルホン酸リチウム	35	重量部
0.3%白金触媒	2.5	重量部

これを平面上に展開して、90℃で1時間加熱して、厚み40μmのゲル状電解質(5)を得た。このゲル状電解質(5)の貯蔵弾性率は、 4.5×10^5 Pa、電気伝導性は、 7.0×10^{-4} S/cmであった。一方、市販のリチウム2次電池より正極層と負極層を取り出し、金属アルミニウム、正極層、ゲル状電解質(5)、※

※負極層、及び金属銅を積層して、リチウム2次電池を0.1mAの電流値で充放電を行ったところ、その容量は、1.8mAh/枚であった。

【0070】実施例6

次の各材料を混合した。

前駆体(3)	149.6	重量部
式(3-1-6)の化合物	17.4	重量部
式(4-1)の化合物	60	重量部
プロピレンカーボネイト	40	重量部
過塩素酸リチウム	27	重量部
0.3%白金触媒	0.8	重量部

これを平面上に展開して、90℃で1時間加熱して、厚み40μmのゲル状電解質(6)を得た。このゲル状電解質(6)の貯蔵弾性率は、 9.5×10^5 Pa、電気伝導性は、 7.0×10^{-4} S/cmであった。一方、市販のリチウム2次電池より正極層と負極層を取り出し、金属アルミニウム、正極層、ゲル状電解質(6)、★

★負極層、及び金属銅を積層して、リチウム2次電池を0.1mAの電流値で充放電を行ったところ、その容量は、1.7mAh/枚であった。

【0071】実施例7

次の各材料を混合した。

式(1-2-1)の化合物	43.5	重量部
式(2-1-1)の化合物	50.2	重量部
式(2-2-1)の化合物	72.6	重量部
式(3-1-1)の化合物	27	重量部
式(4-1)の化合物	60	重量部
エチレンカーボネイト	20	重量部
プロピレンカーボネイト	20	重量部
トリフルオロメタンスルホン酸リチウム	44	重量部
0.3%白金触媒	1.5	重量部

これを平面上に展開して、90℃で1時間加熱して、厚み40μmのゲル状電解質(7)を得た。このゲル状電解質(7)の貯蔵弾性率は、 6.5×10^5 Pa、電気伝導性は、 5.0×10^{-4} S/cmであった。一方、市販のリチウム2次電池より正極層と負極層を取り出し、

0重量部に溶解させ、触媒として塩化白金酸アルコール溶液(3.8×10^{-3} %)を加え、50℃で48時間加熱して、反応生成物を減圧乾燥で取り除き、0重量部過塩素酸リチウムのテトラヒド

(13)

特開2000-

23

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に特定の多官能性化合物を反応させて得られる架橋構造体や、三つ以上のS-H基を有するポリシロキサン化合物と特定のポリアルキレンオキサイド化合物にさらに特定の多官能性化合物を反応させて得られる架橋構造体*

*や、さらにはこれら高分子化合物や架橋変性シリコーンを組み合わせたものは、上したリチウム2次電池に適するゲル状用できた。

フロントページの続き

(72)発明者 池上 幸史郎
東京都千代田区丸の内3丁目4番2号 三菱製紙株式会社内
(72)発明者 兵頭 建二
東京都千代田区丸の内3丁目4番2号 三菱製紙株式会社内
(72)発明者 日野 賢一
東京都千代田区大手町二丁目6番1号 日本ユニカー株式会社内

(72)発明者 鹿野 直樹
東京都千代田区大手町二丁目 本ユニカー株式会社内
(72)発明者 安藤 英治
東京都千代田区大手町二丁目 本ユニカー株式会社内
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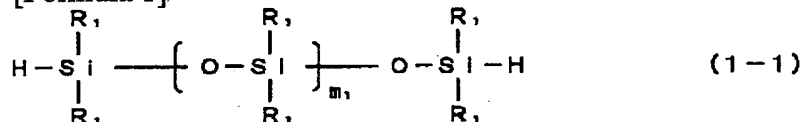
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CLAIMS

[Claim(s)]

[Claim 1] The gel electrolyte for lithium rechargeable batteries characterized by containing at least the high molecular compound which is made to carry out the polymerization of the polysiloxane compound of the following general formula (1-1) which has an Si-H basis, and the polyalkylene oxide compound of a general formula (2-1) to both ends by turns, and is obtained.

[Formula 1]



(R₁ shows among a formula the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually, and m₁ shows the integers from 0 to 500.)

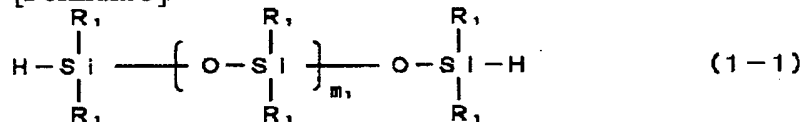
[Formula 2]



(R₂₁ shows among a formula the monovalent hydrocarbon group which has an end double bond, a shows the integer of 2 to 4, and n₂₁ shows one or more integers.)

[Claim 2] The gel electrolyte for lithium rechargeable batteries characterized by containing at least the structure-of-cross-linkage object which the polysiloxane compound of the following general formula (1-1) which has an Si-H basis, the polyalkylene oxide compound of a general formula (2-1), and the polyfunctional compound of a general formula (3-1) are made to react to both ends, and is acquired.

[Formula 3]



(R₁ shows among a formula the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually, and m₁ shows the integers from 0 to 500.)

[Formula 4]



(R₂₁ shows among a formula the monovalent hydrocarbon group which has an end double bond, a shows the integer of 2 to 4, and n₂₁ shows one or more integers.)

[Formula 5]



(Among a formula, R31 shows a hydrogen atom or an alkyl group, and R32 shows a bivalent organic machine or bivalent direct junction.) l3 is two or more integers, and Z31 is a substituent containing carbon or nitrogen, and is a basis with the valence of the same number as l3.

[Claim 3] the polysiloxane which has three or more Si-H bases, and the following general formula (2-1) -- or (2-2) the gel electrolyte for lithium rechargeable batteries characterized by containing at least the structure-of-cross-linkage object which a polyalkylene oxide compound and the polyfunctional compound of a general formula (3-1) are made to react, and is acquired

[Formula 6]



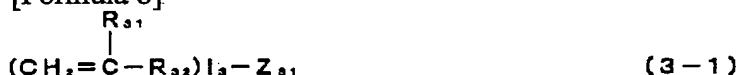
(R21 shows among a formula the monovalent hydrocarbon group which has an end double bond, a shows the integer of 2 to 4, and n21 shows one or more integers.)

[Formula 7]



(R22 shows among a formula the monovalent hydrocarbon group which has an end double bond, R23 shows a hydrogen atom, a monovalent saturated-hydrocarbon machine, or an acyl group, b shows the integer of 2 to 4, and n22 shows one or more integers.)

[Formula 8]



(Among a formula, R31 shows a hydrogen atom or an alkyl group, and R32 shows a bivalent organic machine or bivalent direct junction.) l3 is two or more integers, and Z31 is a substituent containing carbon or nitrogen, and is a basis with the valence of the same number as l3.

[Claim 4] The gel electrolyte for lithium rechargeable batteries characterized by containing at least a high molecular compound according to claim 1 and the denaturation silicone whose viscosity in 40 degrees C is 10000 or less cPs.

[Claim 5] The gel electrolyte for lithium rechargeable batteries characterized by containing at least a structure-of-cross-linkage object according to claim 2 and the denaturation silicone whose viscosity in 40 degrees C is 10000 or less cPs.

[Claim 6] The gel electrolyte for lithium rechargeable batteries characterized by containing at least a structure-of-cross-linkage object according to claim 3 and the denaturation silicone whose viscosity in 40 degrees C is 10000 or less cPs.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the new gel electrolyte for lithium rechargeable batteries, and the new gel electrolyte for lithium rechargeable batteries which was excellent in electrical conductivity in more detail.

[0002]

[Description of the Prior Art] For a lithium rechargeable battery, a theoretical energy density is high, a portable electronic equipment power supply is begun, and the application ranges, such as an electric vehicle and a power supply for power storage, are vast. Since the high solution system of ionic conductivity could not be used for the electrolyte used for the conventional lithium rechargeable battery because of reactivity with an expensive lithium, the organic electrolytic solution which dissolved lithium salt into the nonaqueous solution was used. However, in the organic electrolyte, since it was liquefied, the cell needed to be damaged, or it needed to evaporate by generation of heat at the time of overcharge etc., the risk of explosion always needed to follow, and safety sufficient for the reason needed to be devised, and it had become the badness of the cause by which it raises the cost of a cell again, or user-friendliness.

[0003] On the other hand, recently, the polyelectrolyte, the gel electrolyte, etc. are proposed. These have the outstanding feature equipped with comparatively high ion conductivity, a vast potential window, a good thin film plasticity, flexibility, lightweight nature, elasticity, transparency, etc. In a rechargeable battery, since the volume while many electrode active materials are operating is changed, especially the flexibility and the elastic property of a polyelectrolyte are important. Moreover, it is said that there are also a fall of the cell capacity at the time of the repeat use by desorption of an electrode material and short circuit prevention ability of positive/negative pole material.

[0004] As such a polyelectrolyte, it is Advanced. Various electrolytes are proposed in Materials and 10,439 (1998). Here, it has a polyethylene oxide, the composite of a polyethylene oxide and polysilane and the composite of a polyethylene oxide and poly force FAZEN, and a polyethylene oxide in a structural unit, and the polymer of an epoxy group, an isocyanate machine, and the structure of cross linkage that has siloxane structure further etc. is introduced. Especially the composite with polysiloxane structure is a polyelectrolyte which attracts attention from the low-temperature property being excellent.

[0005] The polyelectrolyte which has a polysiloxane as a structural unit, As a composite with a polyethylene-oxide system compound, it is J. Polym. Sci. Polym. Lett. Ed., 22,659 (1984), Solid Although indicated by StateIonics, 15,233 (1985), JP,63-136409,A, JP,8-21389,B, JP,8-78053,A, etc. A problem is not in own stability of a compound, the structure-of-cross-linkage object whose lamination suppresses desorption of an electrode material and becomes possible is not acquired, or that sufficient ion conductivity is not obtained etc. poses a problem, and it has not yet resulted in utilization.

[0006]

[Problem(s) to be Solved by the Invention] The technical problem of this invention cancels the trouble that the polyelectrolyte which it has as a structural unit has the conventional polysiloxane, and is to offer the new gel electrolyte suitable for the lithium rechargeable battery.

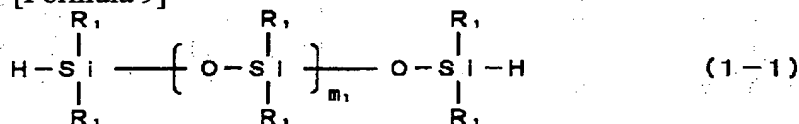
[0007]

[Means for Solving the Problem] The high molecular compound obtained by carrying out the polymerization of the specific polysiloxane compound which has an Si-H basis, and the specific polyalkylene oxide compound to both ends by turns as a result of repeating examination wholeheartedly that this invention persons should solve the above-mentioned technical problem, The structure-of-cross-linkage object which a further specific polyfunctional compound is made to react to these polysiloxanes compound and a polyalkylene oxide compound, and is acquired, The structure-of-cross-linkage object which a further specific polyfunctional compound is made to react to the polysiloxane compound which has three or more Si-H bases, and a specific polyalkylene oxide compound, and is acquired, What furthermore combined specific denaturation silicone with these high molecular compounds or the structure-of-cross-linkage object found out that it could be used as a gel electrolyte suitable for the lithium rechargeable battery. this invention results in completion based on these knowledge.

[0008] That is, according to this invention, the gel electrolyte for lithium rechargeable batteries characterized by containing at least the high molecular compound which is made to carry out the polymerization of the polysiloxane compound of the following general formula (1-1) which has an Si-H basis, and the polyalkylene oxide compound of a general formula (2-1) to both ends by turns, and is obtained is offered.

[0009]

[Formula 9]



(R1 shows among a formula the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually, and m1 shows the integers from 0 to 500.)

[0010]

[Formula 10]

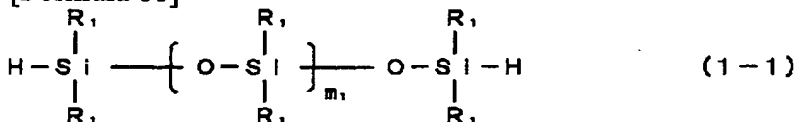


(R21 shows among a formula the monovalent hydrocarbon group which has an end double bond, a shows the integer of 2 to 4, and n21 shows one or more integers.)

[0011] Moreover, according to this invention, the gel electrolyte for lithium rechargeable batteries characterized by containing at least the structure-of-cross-linkage object which the polysiloxane compound of the following general formula (1-1) which has an Si-H basis, the polyalkylene oxide compound of a general formula (2-1), and the polyfunctional compound of a general formula (3-1) are made to react to both ends, and is acquired is offered.

[0012]

[Formula 11]



(R1 shows among a formula the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually, and m1 shows the integers from 0 to 500.)

[0013]

[Formula 12]



(R21 shows among a formula the monovalent hydrocarbon group which has an end double bond, a shows the integer of 2 to 4, and n21 shows one or more integers.)

[0014]

[Formula 13]



(Among a formula, R31 shows a hydrogen atom or an alkyl group, and R32 shows a bivalent organic machine or bivalent direct junction.) l3 is two or more integers, and Z31 is a substituent containing carbon or nitrogen, and is a basis with the valence of the same number as l3.

[0015] furthermore, the polysiloxane which has three or more Si-H bases according to this invention and the following general formula (2-1) -- the gel electrolyte for lithium rechargeable batteries characterized by containing at least the structure-of-cross-linkage object which a polyalkylene oxide compound and the polyfunctional compound of a general formula (3-1) are made to react, and is acquired is offered for or (2-2)

[0016]

[Formula 14]



(R21 shows among a formula the monovalent hydrocarbon group which has an end double bond, a shows the integer of 2 to 4, and n21 shows one or more integers.)

[0017]

[Formula 15]



(R22 shows among a formula the monovalent hydrocarbon group which has an end double bond, R23 shows a hydrogen atom, a monovalent saturated-hydrocarbon machine, or an acyl group, b shows the integer of 2 to 4, and n22 shows one or more integers.)

[0018]

[Formula 16]



(Among a formula, R31 shows a hydrogen atom or an alkyl group, and R32 shows a bivalent organic machine or bivalent direct junction.) l3 is two or more integers, and Z31 is a substituent containing carbon or nitrogen, and is a basis with the valence of the same number as l3.

[0019] According to this invention, the gel electrolyte for lithium rechargeable batteries characterized by containing at least the above-mentioned high molecular compound or the structure-of-cross-linkage object of one of the above, and the denaturation silicone whose viscosity in 40 degrees C is 10000 or less cPs is offered further again.

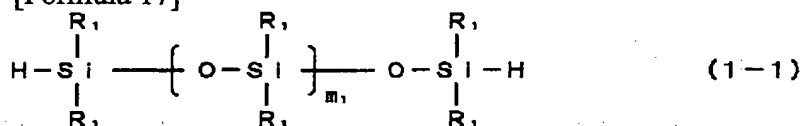
[0020]

[Embodiments of the Invention] Hereafter, this invention is explained in detail. The high molecular compound or structure-of-cross-linkage object of this invention is the material which can form a high order structure-of-cross-linkage object or the amount structure of macromolecules, in order to make an electrolyte gel, and a solid polymer electrolyte acquires it. And each of these matter carries out the polymerization of the raw material in the state of a monomer or oligomer by the hydrosilylation reaction, and is produced. A hydrosilylation reaction is an addition reaction to which the compound which has ARUKENIRU machines, such as an allyl compound and a vinyl, and the polysiloxane

compound which has an Si-H basis react, and compounds, such as platinum, a ruthenium, a rhodium, palladium, an osmium, and iridium, are known as the catalyst. However, a platinum compound is useful from conditions, such as having the high activity for a reaction advancing quickly and a reaction being completed, not causing a resultant and a secondary reaction, and not affecting a cell property, being required of this invention. As an example of a platinum compound, the thing which made support, such as a chloroplatinic acid, a simple substance of platinum, an alumina, a silica, and carbon black, support solid-state platinum, a platinum-vinyl siloxane complex, a platinum-phosphine complex, a platinum-force fight complex, a platinum alcoholate catalyst, etc. are mentioned. A platinum catalyst is usually added about 0.1% of the weight from 0.0001 % of the weight in the case of a hydrosilylation reaction. Moreover, since the temperature dependence of a reaction rate is large, this reaction can carry out heating and can promote a reaction. This is the big advantage of a hydrosilylation reaction, and if afterbaking of the reactant is mixed, fabricated and carried out on moderate viscosity, the gel object of a desired configuration will be obtained at a stretch. Moreover, they are other by-products, such as water, and the technique of almost not having the volume change immediately after a reaction, and having been excellent as the gelling method for cells at this time. [0021] As one mode of this invention, using a hydrosilylation reaction, polysiloxane structure and polyalkylene oxide structure enter by turns, and the compound which is a macromolecule is obtained. The polysiloxane compound first shown by hydrolysis of a dimethyldichlorosilane and a dimethyl chlorosilane and hydrolysis of dimethoxy dimethylsilane and a JIMETOKISHIMI methylsilane as the synthetic method of such the structure by the following general formula (1-1) which has an Si-H basis in both ends, for example is obtained. At this time, the molecular weight of a polysiloxane compound is changeable by changing the charge of a monomer which has an Si-H basis.

[0022]

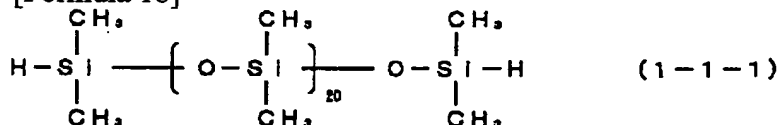
[Formula 17]



R1 shows among a formula the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually. m1 -- the integers from 0 to 500 -- it is -- desirable -- the integers from 2 to 100 -- it is about five to 30 integer still more preferably Specifically as this polysiloxane compound, there is a compound shown by the following formula (1-1-1) whose m1 R1 is a methyl group and is 20.

[0023]

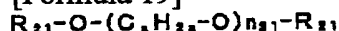
[Formula 18]



[0024] Next, if the chain polymerization of the ethyleneoxide etc. is carried out to dialcohol objects, such as ethylene glycol, in the ring opening reaction of an epoxy group, the polyalkylene glycol which has a hydroxyl group in both ends will be obtained. For example, the hydroxyl group of the both ends of the polyalkylene glycol obtained in this way is replaced by the vinyloxy machine, the aryloxy group, or 2-methyl allyloxy machine, and the polyalkylene oxide compound shown by the following general formula (2-1) which has an alkylene machine in both ends is obtained. Under the present circumstances, although an oxyethylene unit independent is sufficient like a polyethylene oxide, the polymerization of the units, such as an oxyethylene machine, a methyloxy ethylene, and an ethyloxy ethylene, can be carried out to random or the letter of a block, and this can also be used as a polyalkylene oxide compound.

[0025]

[Formula 19]



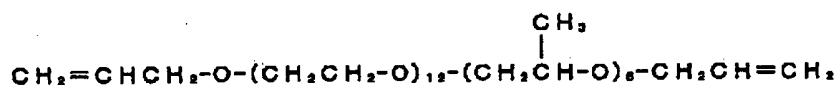
(2-1)

R21 shows among a formula the monovalent hydrocarbon group which has an end double bond, a shows the integer of 2 to 4, and n21 shows one or more integers. In this case, as an example of R21, it is CH₂=CHCH₂-, CH₂=CHCH₂CH₂-, CH₂=CH-, CH₂=C(CH₃)CH₂-, CH₂=CHC(CH₃)H-, etc., and is CH₂=CHCH₂- preferably. Moreover, as a desirable range of n21, it is 4 to about 20. Specifically as this polyalkylene oxide compound, there is a compound shown by the formula (2-1-1).

[0026]

[Formula 20]

(2-1-1)

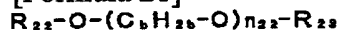


[0027] Thus, the polysiloxane compound of the produced general formula (1-1) and the polyalkylene oxide compound of a general formula (2-1) are heated by the hydrosilylation reaction also as a catalyst, and a polymerization is carried out. A polymerization continues until a reactional phase hand is no longer found out, and the purpose compound (1) of this invention is obtained. If the above-mentioned polysiloxane compound and a polyalkylene oxide compound set an Si-H basis to 1, they will be mixed by the ratio to which an alkenyl machine becomes 0.8 to about 1.2 from 0.5 preferably about two. If the polyalkylene oxide compound is superfluous at this time, an alkenyl machine will remain in both ends, and if the polysiloxane compound is conversely superfluous, an Si-H basis remains in both ends. And it depends on the preparation concentration of a reactant etc. for the average molecular weight of the purpose compound (1) obtained.

[0028] Moreover, if what carried out alkoxy denaturation of the piece end of the polyalkylene oxide section (compound shown by the below-mentioned general formula (2-2)) is added, this serves as the last polymerization edge and can control the average molecular weight by this. Thus, the obtained purpose compound (1) has polysiloxane structure and polyalkylene oxide structure by turns, and the number of repeat structures is 4 to about 80 preferably about 100 from 2. As the manufacture method of the compound which carried out alkoxy denaturation of the piece end of this polyalkylene oxide section, the polymerization of the ***** which has epoxy groups, such as an ethyleneoxide, is carried out to alcohol, such as a methanol, ethanol, and a butanol, by ring opening polymerization, for example, and the polyalkylene oxide which has a hydroxyl group at one end is obtained. Thus, the compound shown by the obtained following general formula (2-2) is a polyalkylene oxide compound with which the hydroxyl group in one end of polyalkylene oxide is replaced by the vinyloxy machine, the aryloxy group, or 2-methyl allyloxy machine, it has an alkenyl machine in one side, and alkoxy denaturation of the piece end was carried out.

[0029]

[Formula 21]



(2-2)

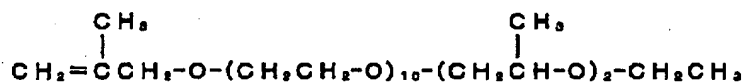
R22 shows among a formula the hydrocarbon group which has an end double bond, R23 shows a hydrogen atom, a monovalent saturated-hydrocarbon machine, or an acyl group, b shows the integer of 2 to 4, and n22 shows one or more integers. In this case, as an example of R22, there are CH₂=CHCH₂-, CH₂=CHCH₂CH₂-, CH₂=CH-, CH₂=C(CH₃)CH₂-, CH₂=CHC(CH₃)H-, etc., and they are CH₂=CHCH₂- and CH₂=C(CH₃)CH₂- preferably. As a desirable range of n22, it is 4 to about 20. As an example of the monovalent saturated-hydrocarbon machine in R23, the alkyl group of the carbon numbers 1-18, such as a methyl group and an ethyl group, etc. is mentioned. As a desirable example of R23, they are a hydrogen atom, a methyl group, an ethyl group, a butyl, or an acyl group.

Specifically as a polyalkylene oxide compound with which alkoxy denaturation of this piece end was carried out, there is a compound shown by the following formula (2-2-1).

[0030]

[Formula 22]

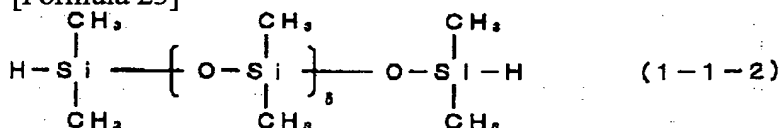
(2-2-1)



[0031] Next, the structure-of-cross-linkage object which mixes the polyalkylene oxide compound of the general formula (2-1) which has an alkylene machine, and the polyfunctional compound (polyfunctional compound shown by the below-mentioned general formula (3-1)) for forming the structure of cross linkage to both ends, and is acquired by the polysiloxane compound of the general formula (1-1) which has an Si-H basis in both ends by the hydrosilylation reaction as another mode of this invention is the purpose compound (2) of this invention. When the compound of a formula (1-1), the compound of a formula (2-1), and the compound of a formula (3-1) set the Si-H basis of the compound of a formula (1-1) to 1 at this time, the alkenyl machine of the compound of a formula (2-1) makes it react by the ratio from which 0.1 to about 1.99 and the alkenyl machine of the compound of a formula (3-1) become 0.01 to about 1.99. When producing the purpose compound (2), as a polysiloxane compound of a formula (1-1), m1 is desirable and zero to 50 or less integer and the thing which is one to 20 or less integer still more preferably are desirable. Specifically as a compound applicable to this, there is a compound shown by the following formula (1-1-2).

[0032]

[Formula 23]



[0033] Although the polyfunctional compound used for producing the purpose compound (2) is shown by the following general formula (3-1), this polyfunctional compound has three or more unsaturation hydrocarbon groups, causes the Si-H basis of the compound of a formula (1-1) or the Si-H basis of the reactant of the compound of a formula (1-1), and the compound of a formula (2-1), and the same hydrosilylation reaction as the above, and forms a structure-of-cross-linkage object.

[0034]

[Formula 24]

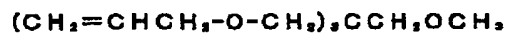


Among a formula, R31 shows alkyl groups, such as a hydrogen atom or a methyl group, and an ethyl group, and is a hydrogen atom or a methyl group preferably. R32 shows a bivalent machine or direct coupling, and has a methylene group, an ethylene, a phenylene group, etc. as an example of a bivalent organic machine. l3 is two or more integers, and is 3 or 4 preferably. Z31 is a substituent containing carbon or nitrogen, and is a basis with the same valence as l3. As a thing applicable to this polyfunctional compound The formula (3-1-1) specifically shown below, a formula (3-1-2), a formula (3-1-3), There is a compound of a formula (3-1-4), a formula (3-1-5), a formula (3-1-6), a formula (3-1-7), a formula (3-1-8), a formula (3-1-9), a formula (3-1-10), a formula (3-1-11), or a formula (3-1-12) etc.

[0035]

[Formula 25]

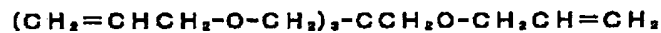
(3-1-1)



[0036]

[Formula 26]

(3-1-2)



[0037]

[Formula 27]

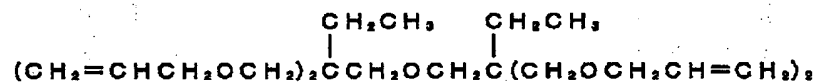
(3-1-3)



[0038]

[Formula 28]

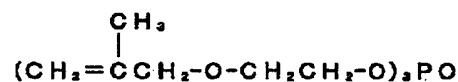
(3-1-4)



[0039]

[Formula 29]

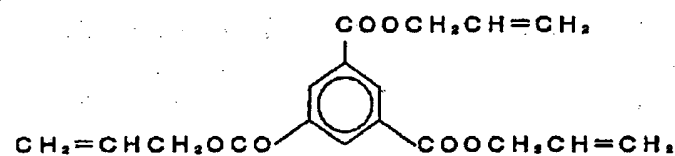
(3-1-5)



[0040]

[Formula 30]

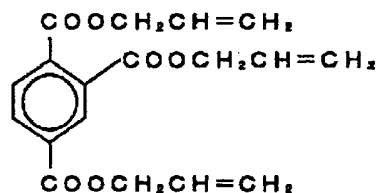
(3-1-6)



[0041]

[Formula 31]

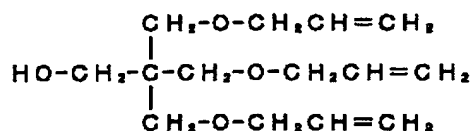
(3-1-7)



[0042]

[Formula 32]

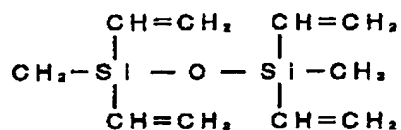
(3-1-8)



[0043]

[Formula 33]

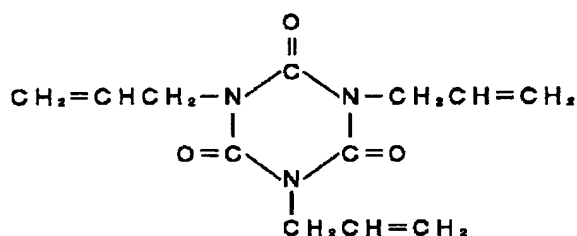
(3-1-9)



[0044]

[Formula 34]

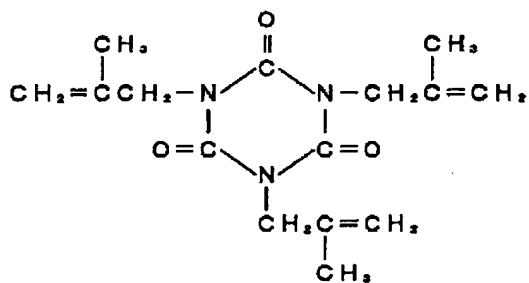
(3-1-10)



[0045]

[Formula 35]

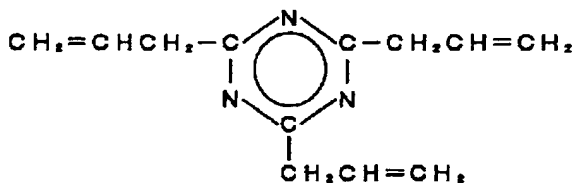
(3-1-11)



[0046]

[Formula 36]

(3-1-12)



[0047] When obtaining the purpose compound (2), the polyfunctional compound of a general formula (3-1) has further the polysiloxane compound of a general formula (1-1), the polyalkylene oxide compound of a general formula (2-1), and the case where the compatibility between each compound

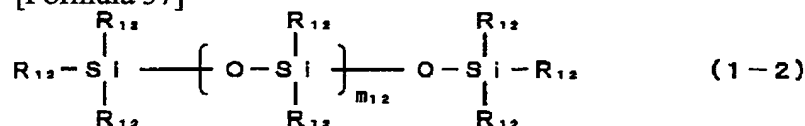
becomes remarkably bad, from the relation of molecular weight etc. In this case, the compound of a general formula (2-1) can be made to be able to react by the hydrosilylation reaction in the superfluous state of the compound of a general formula (1-1) beforehand, a precursor with moderate molecular weight can be produced, the polyfunctional compound of a general formula (3-1) can be made to be able to act on this, and a structure-of-cross-linkage object can also be acquired.

Specifically, if the Si-H basis of the compound of a general formula (1-1) is set to 1, make the alkenyl machine of the compound of a general formula (2-1) react by the ratio which becomes 0.1 to about 1.99, and will produce a precursor, the alkenyl machine of the polyfunctional compound of a general formula (3-1) will be made to react further by the ratio which becomes 0.01 to about 1.9, and it will obtain.

[0048] Next, the structure-of-cross-linkage object reacted and acquired as still more nearly another mode of this invention in the polysiloxane which has three or more Si-H bases, the polyalkylene oxide compound of a general formula (2-1) or a formula (2-2), and the polyfunctional compound of a general formula (3-1) is the purpose compound (3) of this invention. There is a straight chain-like polysiloxane shown by the general formula (1-2) shown below as a polysiloxane which has three or more Si-H bases, an annular polysiloxane shown by the general formula (1-3), or a ladder-like polysiloxane shown by the general formula (1-4).

[0049]

[Formula 37]

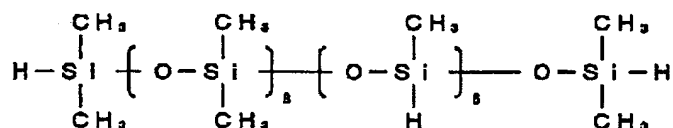


Among a formula, although R₂₁ shows the monovalent hydrocarbon group or monovalent hydrogen atom which does not include an aliphatic unsaturation independently mutually, three [of a molecule] or more of R₁₂ are a hydrogen atom, and 50 or less pieces are 3 to about ten desirable still more preferably. m₁₂ shows the integer of 0 to 500. The desirable range of m₁₂ is 2 to about 100, and is 5 to about 30 still more preferably. In addition, specifically as a compound applicable to this, there is a compound of the following formula (1-2-1).

[0050]

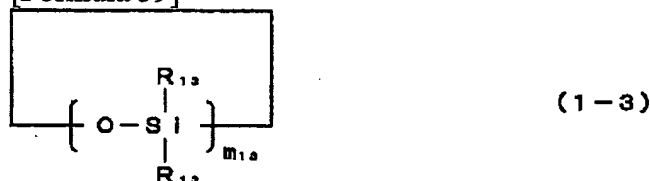
[Formula 38]

(1-2-1)



[0051]

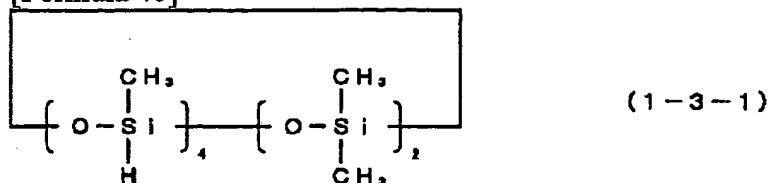
[Formula 39]



R₁₃ shows among a formula a hydrogen atom or the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually, and three in a molecule to eight of R₁₃ pieces are hydrogen atoms. m₁₃ shows the integer of 3 to 8. In addition, specifically as a compound applicable to this, there is a compound of the following formula (1-3-1).

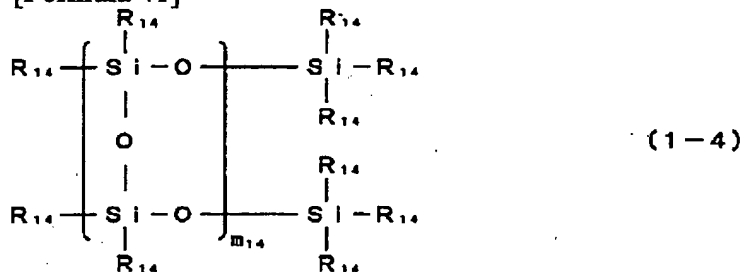
[0052]

[Formula 40]



[0053]

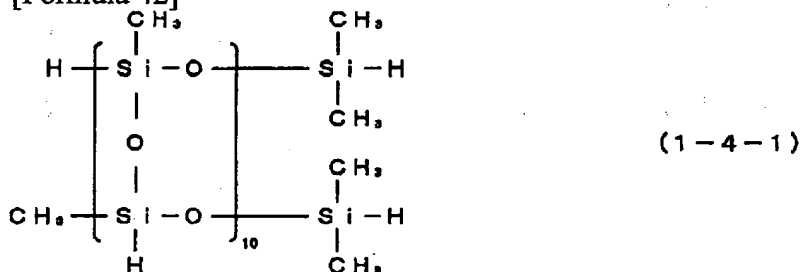
[Formula 41]



R₁₄ shows among a formula a hydrogen atom or the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually, three [of a molecule] or more of R₁₄ are a hydrogen atom, and they are 50 or less pieces preferably. m₁₄ is the integers from 1 to 50, and is 4 to about 20 still more preferably about 30 from 2 preferably. In addition, specifically as a compound applicable to this, there is a compound of the following formula (1-4-1).

[0054]

[Formula 42]



[0055] If the Si-H basis of the polysiloxane which has such three or more Si-H bases is set to 1, the purpose compound (3) of this invention By the ratio from which the alkenyl machine of the compound of a general formula (2-1) becomes 0.1 to about 0.99, or the ratio from which the alkenyl machine of the compound of a general formula (2-2) becomes 0.1 to about 0.9 Furthermore, it is obtained by making it react by the ratio from which the alkenyl machine of the compound of a general formula (3-1) becomes 0.01 to about 0.8. Moreover, it obtains, and it can continue, a precursor can be made to make the polysiloxane which has three or more Si-H bases beforehand, the compound of a general formula (2-1), and the compound of a general formula (2-1) react by such ratio like the time of obtaining the purpose compound (2) as an option, and to be able to react with the compound of a general formula (3-1), and it can also obtain.

[0056] The purpose compound (1) mentioned above The gel electrolyte containing either and denaturation silicone of - (3) is also one mode of this invention. Denaturation silicone here means polyether denaturation silicone, polyester denaturation silicone, etc. of denaturation silicone, such as alkoxy denaturation silicone, alcoholic denaturation silicone, carboxy denaturation silicone, epoxy denaturation silicone, and amino denaturation silicone, the shape of the shape of a pendant, and a straight chain, piece end denaturation, and both-ends denaturation. Although such viscosity is 10000 or less cPs at 40 degrees C, it is 1000 or less cPs still more preferably 2000 or less cPs preferably. if it

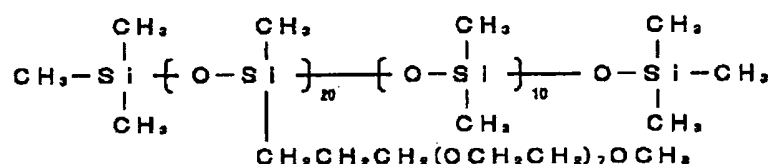
sets the purpose compound to 1 as the ratio in mixing either and these denaturation silicone of purpose compound (1) - (3) -- denaturation silicone -- a 0.01 to 100-fold quantitative-ratio grade -- it is preferably mixed and used by 0.1 to 10-fold quantitative-ratio grade

[0057] Especially as denaturation silicone used, polyether denaturation silicone is desirable and denaturalizes in the shape of a pendant more preferably. Specifically as desirable denaturation silicone, what is shown by a following formula (4-1) and a following formula (4-2) is mentioned. When the viscosity of the denaturation silicone of this formula (4-1) was measured by the Brookfield viscometer (the rotor number 2, rotational frequency 60rpm) by Tokyo Keiki Co., Ltd. which is a rotational viscometer, it was 173cP(s) at 40 degrees C.

[0058]

[Formula 43]

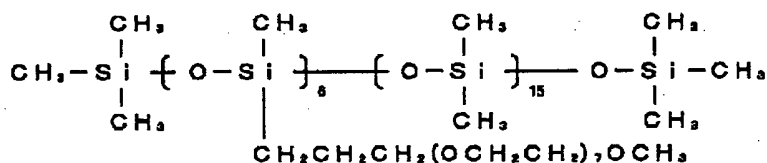
(4-1)



[0059]

[Formula 44]

(4-2)



[0060] this invention is used, after combining the arbitrary material of the various common knowledge for a lithium rechargeable battery operating good with the amount structure of macromolecules or the structure-of-cross-linkage object mentioned above, since it is related with the electrolyte of a lithium rechargeable battery. First, a supporting electrolyte is required in order to operate as an electrolyte. as a supporting electrolyte -- LiClO₄, LiBF₄, LiAsF₆, LiCF₃SO₃, Li (CF₃SO₂)₂N, and Li (CF₃SO₂)₃ -- lithium salt, such as C and LiBPh₄ (Ph shows a phenyl group here), can be used Moreover, the solvent for dissolving lithium salt can also be used. As a solvent which can be used, it is independent, or ether system compounds, such as ester system compound [which has carbonyl combination of propylene carbonate, ethylene carbonate gamma-butyrolactone, dimethyl carbonate, diethyl carbonate, etc.], tetrahydrofuran, 1, 2-dimethoxyethane, 1, 2-ethoxy ethane, 1, and 3-dioxane, etc. can be mixed and used. Furthermore, ion conductivity polymer, such as denaturation poly force FAZEN which has the denaturation polyacrylate and polyacrylonitrile which have polyalkylene oxide compounds, such as a tetraethylene-glycol wood ether and a tetrapropylene glycol wood ether, the denaturation poly dimethylsiloxane which has polyalkylene oxide in a side chain, and polyalkylene oxide in a structural unit, a polyvinylidene fluoride, and polyalkylene oxide in a structural unit, is also mixable.

[0061] In order to use it as the polyelectrolyte or gel electrolyte for lithium rechargeable batteries, beforehand, the precursor of a structure-of-cross-linkage object or the amount structure of macromolecules and the lithium salt as a supporting electrolyte are inserted at least, it is made to gel beforehand and there are a method of making this gelling by the hydrosilylation reaction, and a method of making each electrode material rival after that between positive/negative electrode materials. In order to maintain the intensity of gel at this time, a nonwoven fabric sheet, a porosity film, etc. can also be used. As a nonwoven fabric sheet, electrolytic retentivity is excellent first, to the

ion conductivity of the high molecular compound produced further or a gel electrolyte, it is low resistance and the thing excellent in electrolytic retentivity can be used. As the manufacture method of a nonwoven fabric, wet or dry-type all can be used, and the amount of eyes is two or less 100 g/m, and is 5-50g/m² preferably. As a fiber material used, although it is polyester, polypropylene, polyethylene, Teflon (registered trademark), etc., it is not necessarily limited to especially these. As a porosity film, the film which porosity-sized films, such as polyethylene and polypropylene, to uniaxial stretching etc. is used, for example. As a weight, a 5 g/m² to about two 30 g/m thing is used.

[0062] With the positive-electrode material used for a lithium rechargeable battery the shape of LiCoO₂, LiNiO₂, spinel type LiMn₂O₄, and amorphous -- the mixture of V₂O₅, beta-MnO₂, and Li₂MnO₃ -- Organic disulfide compounds, such as 4, 2, 5-dimercapto-3, and 4-thiadiazole, etc. are made into a positive active material. Li₄ / 3Mn₅/3O of a spinel superstructure -- This is made powdered and electric conduction agents, such as acetylene black, the thickener which consists of an organic high molecular compound are added. Positive-electrode material is applied on the aluminum which is a positive-electrode charge collector, and is used as porosity.

[0063] With negative-electrode material, in the case of a metal, negative-electrode active materials, such as a metal lithium, a lithium aluminium alloy, a Li-Pb-Cd-In alloy, and a lithium and a graphite compound, a lithium and a difficulty graphitized-carbon compound, a lithium and an amorphous tin multiple oxide, an amorphous cobalt substitution lithium nitride, are plated to a nickel board etc., in other cases, it is made powdered like positive-electrode material, and electric conduction agents, such as acetylene black, the thickener which consists of an organic macromolecule are added. Like the latter, in the case of-like [paste], it is applied on collecting electrode plates, such as copper, and it is used as porosity.

[0064]

[Example] Hereafter, although an example explains this invention in detail further, unless the main point of this invention is exceeded, it is not limited to these.

[0065] Each material of the primary example was mixed.

The compound of a formula (1-1-1) The compound of a 160 weight sections type (2-1-1) 97 weight sections propylene carbonate 100 weight sections lithium perchlorate 0.3% platinum catalyst of 36 weight sections the 2.5 weight sections -- this -- the amount of eyes of 15g/m² -- a nonwoven fabric with a thickness of 30 micrometers -- sinking in -- 90 degrees C -- 1 hour -- heating . The gel electrolyte (1) with a thickness of 32 micrometers was obtained. The storage modulus of this gel electrolyte (1) was 8.5x10³Pa, and electrical conductivity was 6.5x10⁻⁴ S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (1), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 1.8 mAh/cm².

[0066] Each material of the secondary example was mixed.

The compound of a formula (1-1-2) The 67.3 weight sections The compound of a formula (2-1-1) The 84.1 weight sections The compound of a formula (3-1-1) The 13.7 weight sections Ethylene carbonate 40 weight sections Propylene carbonate 60 weight sections Trifluoromethane sulfonic-acid lithium The 39.8 weight sections 0.3% platinum catalyst the 1.2 weight sections -- this -- amount of eyes 15 g/m² -- a nonwoven fabric with a thickness of 30 micrometers -- sinking in -- 90 degrees C -- 1 hour -- heating . The gel electrolyte (2) with a thickness of 32 micrometers was obtained. The storage modulus of this gel electrolyte (2) was 0.9x10⁵Pa, and electrical conductivity was 8.0x10⁻⁴ S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (2), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 1.8 mAh/cm².

[0067] Each material of the 3rd example was mixed, it heated at 100 degrees C for 30 minutes, and the precursor (3) was produced.

compound of a formula (1-1-2) The 67.3 weight sections Compound of a formula (2-1-1) The 84.1 weight sections 0.3% platinum catalyst the 1.4 weight sections -- next, each following compound was mixed with the above-mentioned precursor (3)

A precursor (3) The 151.4 weight sections The compound of a formula (3-1-1) 13.7 Weight section Ethylene carbonate 40 weight sections Propylene carbonate 60 weight sections trifluoromethane sulfonic-acid lithium The 39.8 weight sections 0.3% platinum catalyst the 1.2 weight sections -- this -- amount of eyes 15 g/m² -- a nonwoven fabric with a thickness of 30 micrometers -- sinking in -- 90 degrees C -- 1 hour -- heating . The gel electrolyte (3) with a thickness of 32 micrometers was obtained. The storage modulus of this gel electrolyte (3) was 1.5×10^5 Pa, and electrical conductivity was 7.5×10^{-4} S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (3), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 1.9 mAh/cm².

[0068] Each material of the 4th example was mixed, it heated at 100 degrees C for 30 minutes, and the precursor (4) was produced.

The compound of a formula (1-2-1) The 43.5 weight sections The compound of a formula (2-1-1) The 50.2 weight sections The compound of a formula (2-2-2) The 72.6 weight sections The compound of a formula (3-1-6) The 21.2 weight sections Ethylene carbonate 50 weight sections Dimethoxyethane 50 weight sections Lithium perchlorate 28 weight sections 0.3% platinum catalyst the 2.5 weight sections -- this -- the amount of eyes of 15g/m² -- a nonwoven fabric with a thickness of 30 micrometers -- sinking in -- 90 degrees C -- 1 hour -- heating . The gel electrolyte (4) with a thickness of 32 micrometers was obtained. The storage modulus of this gel electrolyte (4) was 1.4×10^5 Pa, and electrical conductivity was 6.0×10^{-4} S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (4), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 2.0 mAh/cm².

[0069] Each material of the 5th example was mixed.

The compound of a formula (1-1-1) 160 Weight section The compound of a formula (2-1-1) 97 Weight section The compound of a formula (4-1) 100 The weight section Trifluoromethane sulfonic-acid lithium 35 weight sections 0.3% platinum catalyst the 2.5 weight sections -- this -- a flat-surface top -- developing . It heated at 90 degrees C for 1 hour, and the gel electrolyte (5) with a thickness of 40 micrometers was obtained. The storage modulus of this gel electrolyte (5) was 4.5×10^5 Pa, and electrical conductivity was 7.0×10^{-4} S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (5), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 1.8 mAh/cm².

[0070] Each material of the 6th example was mixed.

A precursor (3) The 149.6 weight sections The compound of a formula (3-1-6) The 17.4 weight sections The compound of a formula (4-1) 60 weight sections Propylene carbonate 40 weight sections Lithium perchlorate 27 weight sections 0.3% platinum catalyst the 0.8 weight sections -- this -- a flat-surface top -- developing . It heated at 90 degrees C for 1 hour, and the gel electrolyte (6) with a thickness of 40 micrometers was obtained. The storage modulus of this gel electrolyte (6) was 9.5×10^5 Pa, and electrical conductivity was 7.0×10^{-4} S/cm. On the other hand, the positive-electrode

layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (6), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 1.7 mAh/cm².

[0071] Each material of the 7th example was mixed.

The compound of a formula (1-2-1) The 43.5 weight sections The compound of a formula (2-1-1)

The 50.2 weight sections The compound of a formula (2-2-1) The 72.6 weight sections The compound of a formula (3-1-1) 27 weight sections The compound of a formula (4-1) 60 weight sections Ethylene carbonate 20 weight sections Propylene carbonate 20 weight sections

Trifluoromethane sulfonic-acid lithium 44 weight sections 0.3% platinum catalyst the 1.5 weight sections -- this -- a flat-surface top -- developing . It heated at 90 degrees C for 1 hour, and the gel

electrolyte (7) with a thickness of 40 micrometers was obtained. The storage modulus of this gel electrolyte (7) was 6.5×10^5 Pa, and electrical conductivity was 5.0×10^{-4} S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (7), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 1.8 mAh/cm².

[0072] The example poly methyl hydrogen siloxane of comparison (average molecular weight 300000) 60 weight section, the polyethylene-glycol monoallyl ether 351 weight section, and the tetrapod ethylene GUREKORU diaryl ether 13.7 weight section were dissolved in the toluene 4000 weight section, the isopropyl alcohol solution (3.8×10^{-3} to 3×10^{-2} mol/l.) 80 weight section of a chloroplatinic acid was added as a catalyst, and it heated at 50 degrees C for 48 hours. Next, toluene was removed by reduced pressure drying and the resultant was obtained. In addition to the resultant which produced the tetrahydrofuran solution of a lithium perchlorate 10% of the weight, and produced 40 weight sections previously on the other hand, the tetrahydrofuran was removed for swelling to waiting and the degree, and the electrical conductivity was measured. Consequently, the value of 0.9×10^{-4} S/cm was acquired at the room temperature.

[0073]

[Effect of the Invention] Carry out the polymerization of the specific polysiloxane compound which was obtained by this invention and which has an Si-H basis in both ends, and the specific polyalkylene oxide compound by turns as you explained above. The structure-of-cross-linkage object which a further specific polyfunctional compound is made to react to the high molecular compound obtained, and these polysiloxanes compound and a polyalkylene oxide compound, and is acquired, The structure-of-cross-linkage object which a further specific polyfunctional compound is made to react to the polysiloxane compound which has three or more Si-H bases, and a specific polyalkylene oxide compound, and is acquired, What furthermore combined specific denaturation silicone with these high molecular compounds or the structure-of-cross-linkage object has been used as a gel electrolyte suitable for the lithium rechargeable battery which improved.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] This invention relates to the new gel electrolyte for lithium rechargeable batteries, and the new gel electrolyte for lithium rechargeable batteries which was excellent in electrical conductivity in more detail.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] A theoretical energy density is high, a lithium rechargeable battery begins a portable electronic equipment power supply, and the application ranges, such as an electric vehicle and a power supply for power storage, are wide. Since the high solution system of ionic conductivity could not be used for the electrolyte used for the conventional lithium rechargeable battery because of reactivity with an expensive lithium, the organic electrolytic solution which dissolved lithium salt into the nonaqueous solution was used. However, in the organic electrolyte, since it was liquefied, the cell needed to be damaged, or it needed to evaporate by generation of heat at the time of overcharge etc., the risk of explosion always needed to follow, edfety sufficient for the reason needed to be devised, and it had become the badness of the cause by which it raises the cost of a cell again, or user-friendliness.

[0003] On the other hand, recently, the polyelectrolyte, the gel electrolyte, etc. are proposed. These have the outstanding feature equipped with comparatively high ion conductivity, a large potential window, good thin film formation nature, flexibility, lightweight nature, elasticity, transparency, etc. In a rechargeable battery, since the volume while many electrode active materials are operating is changed, especially the flexibility and the elastic property of a polyelectrolyte are important. Moreover, it is said that there are also a fall of the cell capacity at the time of the repeat use by desorption of an electrode material and short circuit prevention ability of positive/negative pole material.

[0004] As such a polyelectrolyte, it is Advanced. Various electrolytes are proposed in Materials and 10,439 (1998). Here, it has a polyethylene oxide, the composite of a polyethylene oxide and polysilane and the composite of a polyethylene oxide and poly force FAZEN, and a polyethylene oxide in a structural unit, and the polymer of an epoxy group, an isocyanate machine, and the structure of cross linkage that has siloxane structure further etc. is introduced. Especially the composite with polysiloxane structure is a polyelectrolyte which attracts attention from the low-temperature property being excellent.

[0005] The polyelectrolyte which has a polysiloxane as a structural unit, As a composite with a polyethylene-oxide system compound, it is J. Polym. Sci. Polym.Lett. Ed., 22,659 (1984), Solid Although indicated by StateIonics, 15,233 (1985), JP,63-136409,A, JP,8-21389,B, JP,8-78053,A, etc. A problem is not in own stability of a compound, the structure-of-cross-linkage object whose thin layer-ization suppresses desorption of an electrode material and is attained is not acquired, or that sufficient ion conductivity is not obtained etc. poses a problem, and it has not yet resulted in utilization.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] Carry out the polymerization of the specific polysiloxane compound which was obtained by this invention and which has an Si-H basis in both ends, and the specific polyalkylene oxide compound by turns as you explained above. The structure-of-cross-linkage object which a further specific polyfunctional compound is made to react to the high molecular compound obtained, and these polysiloxanes compound and a polyalkylene oxide compound, and is acquired, The structure-of-cross-linkage object which a further specific polyfunctional compound is made to react to the polysiloxane compound which has three or more Si-H bases, and a specific polyalkylene oxide compound, and is acquired, What furthermore combined specific denaturation silicone with these high molecular compounds or the structure-of-cross-linkage object has been used as a gel electrolyte suitable for the lithium rechargeable battery which improved.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The technical problem of this invention cancels the trouble that the polyelectrolyte which it has as a structural unit has the conventional polysiloxane, and is to offer the new gel electrolyte suitable for the lithium rechargeable battery.

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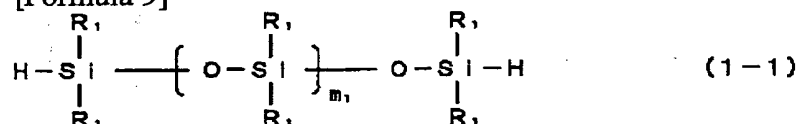
MEANS

[Means for Solving the Problem] The high molecular compound obtained by carrying out the polymerization of the specific polysiloxane compound which has an Si-H basis, and the specific polyalkylene oxide compound to both ends by turns as a result of repeating examination wholeheartedly that this invention persons should solve the above-mentioned technical problem, The structure-of-cross-linkage object which a further specific polyfunctional compound is made to react to these polysiloxanes compound and a polyalkylene oxide compound, and is acquired, The structure-of-cross-linkage object which a further specific polyfunctional compound is made to react to the polysiloxane compound which has three or more Si-H bases, and a specific polyalkylene oxide compound, and is acquired, What furthermore combined specific denaturation silicone with these high molecular compounds or the structure-of-cross-linkage object found out that it could be used as a gel electrolyte suitable for the lithium rechargeable battery. this invention results in completion based on these knowledge.

[0008] That is, according to this invention, the gel electrolyte for lithium rechargeable batteries characterized by containing at least the high molecular compound which is made to carry out the polymerization of the polysiloxane compound of the following general formula (1-1) which has an Si-H basis, and the polyalkylene oxide compound of a general formula (2-1) to both ends by turns, and is obtained is offered.

[0009]

[Formula 9]



(R1 shows among a formula the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually, and m1 shows the integers from 0 to 500.)

[0010]

[Formula 10]

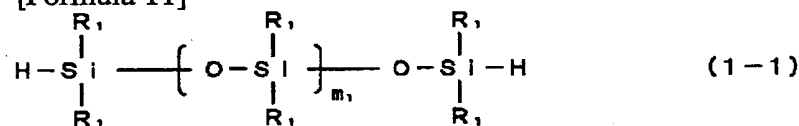


(R21 shows among a formula the monovalent hydrocarbon group which has an end double bond, a shows the integer of 2 to 4, and n21 shows one or more integers.)

[0011] Moreover, according to this invention, the gel electrolyte for lithium rechargeable batteries characterized by containing at least the structure-of-cross-linkage object which the polysiloxane compound of the following general formula (1-1) which has an Si-H basis, the polyalkylene oxide compound of a general formula (2-1), and the polyfunctional compound of a general formula (3-1) are made to react to both ends, and is acquired is offered.

[0012]

[Formula 11]



(R1 shows among a formula the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually, and m1 shows the integers from 0 to 500.)

[0013]

[Formula 12]



(R21 shows among a formula the monovalent hydrocarbon group which has an end double bond, a shows the integer of 2 to 4, and n21 shows one or more integers.)

[0014]

[Formula 13]



(Among a formula, R31 shows a hydrogen atom or an alkyl group, and R32 shows a bivalent organic machine or bivalent direct junction.) l3 is two or more integers, and Z31 is a substituent containing carbon or nitrogen, and is a basis with the valence of the same number as l3.

[0015] furthermore, the polysiloxane which has three or more Si-H bases according to this invention and the following general formula (2-1) -- the gel electrolyte for lithium rechargeable batteries characterized by containing at least the structure-of-cross-linkage object which a polyalkylene oxide compound and the polyfunctional compound of a general formula (3-1) are made to react, and is acquired is offered for or (2-2)

[0016]

[Formula 14]



(R21 shows among a formula the monovalent hydrocarbon group which has an end double bond, a shows the integer of 2 to 4, and n21 shows one or more integers.)

[0017]

[Formula 15]



(R22 shows among a formula the monovalent hydrocarbon group which has an end double bond, R23 shows a hydrogen atom, a monovalent saturated-hydrocarbon machine, or an acyl group, b shows the integer of 2 to 4, and n22 shows one or more integers.)

[0018]

[Formula 16]



(Among a formula, R31 shows a hydrogen atom or an alkyl group, and R32 shows a bivalent organic machine or bivalent direct junction.) l3 is two or more integers, and Z31 is a substituent containing carbon or nitrogen, and is a basis with the valence of the same number as l3.

[0019] According to this invention, the gel electrolyte for lithium rechargeable batteries characterized by containing at least the above-mentioned high molecular compound or the structure-of-cross-linkage object of one of the above, and the denaturation silicone whose viscosity in 40 degrees C is 10000 or less cPs is offered further again.

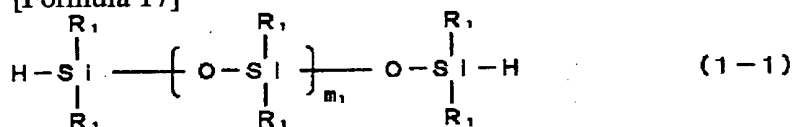
[0020]

[Embodiments of the Invention] Hereafter, this invention is explained in detail. The high molecular compound or structure-of-cross-linkage object of this invention is the material which can form a high order structure-of-cross-linkage object or the amount structure of macromolecules, in order to make an electrolyte gel, and a solid polymer electrolyte acquires it. And each of these matter carries out the polymerization of the raw material in the state of a monomer or oligomer by the hydrosilylation reaction, and is produced. A hydrosilylation reaction is an addition reaction to which the compound which has alkenyl machines, such as an allyl compound and a vinyl, and the polysiloxane compound which has an Si-H basis react, and compounds, such as platinum, a ruthenium, a rhodium, palladium, http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web_cgi_ejje 6/3/2003

an osmium, and iridium, are known as the catalyst. However, a platinum compound is useful from conditions, such as having the high activity for a reaction advancing quickly and a reaction being completed, not causing a resultant and a secondary reaction, and not affecting a cell property, being required of this invention. As an example of a platinum compound, the thing which made support, such as a chloroplatinic acid, a simple substance of platinum, an alumina, a silica, and carbon black, support solid-state platinum, a platinum-vinyl siloxane complex, a platinum-phosphine complex, a platinum-force fight complex, a platinum alcoholate catalyst, etc. are mentioned. A platinum catalyst is usually added about 0.1% of the weight from 0.0001 % of the weight in the case of a hydrosilylation reaction. Moreover, since the temperature dependence of a reaction rate is large, this reaction can carry out heating and can promote a reaction. This is the big advantage of a hydrosilylation reaction, and if afterbaking of the reactant is mixed, fabricated and carried out on moderate viscosity, the gel object of a desired configuration will be obtained at a stretch. Moreover, they are other by-products, such as water, and the technique of almost not having the volume change immediately after a reaction, and having been excellent as the gelling method for cells at this time. [0021] As one mode of this invention, using a hydrosilylation reaction, polysiloxane structure and polyalkylene oxide structure enter by turns, and the compound which is a macromolecule is obtained. The polysiloxane compound first shown by hydrolysis of a dimethyldichlorosilane and a dimethyl chlorosilane and hydrolysis of dimethoxy dimethylsilane and a JIMETOKISHIMI methylsilane as the synthetic method of such the structure by the following general formula (1-1) which has an Si-H basis in both ends, for example is obtained. At this time, the molecular weight of a polysiloxane compound is changeable by changing the charge of a monomer which has an Si-H basis.

[0022]

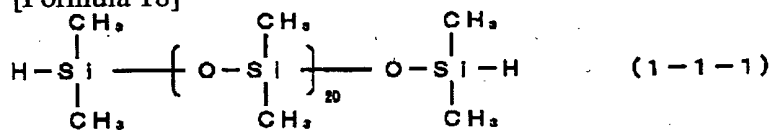
[Formula 17]



R1 shows among a formula the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually. m1 -- the integers from 0 to 500 -- it is -- desirable -- the integers from 2 to 100 -- it is about five to 30 integer still more preferably Specifically as this polysiloxane compound, there is a compound shown by the following formula (1-1-1) whose m1 R1 is a methyl group and is 20.

[0023]

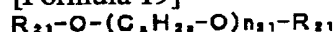
[Formula 18]



[0024] Next, if the chain polymerization of the ethyleneoxide etc. is carried out to dialcohol objects, such as ethylene glycol, in the ring opening reaction of an epoxy group, the polyalkylene glycol which has a hydroxyl group in both ends will be obtained. For example, the hydroxyl group of the both ends of the polyalkylene glycol obtained in this way is replaced by the vinyloxy machine, the aryloxy group, or 2-methyl allyloxy machine, and the polyalkylene oxide compound shown by the following general formula (2-1) which has an alkylene machine in both ends is obtained. Under the present circumstances, although an oxyethylene unit independent is sufficient like a polyethylene oxide, the polymerization of the units, such as an oxyethylene machine, a methyloxy ethylene, and an ethyloxy ethylene, can be carried out to random or the letter of a block, and this can also be used as a polyalkylene oxide compound.

[0025]

[Formula 19]



(2-1)

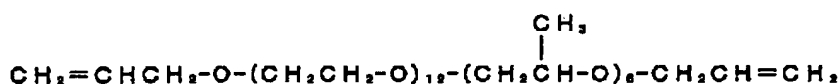
R21 shows among a formula the monovalent hydrocarbon group which has an end double bond, a

shows the integer of 2 to 4, and n21 shows one or more integers. In this case, as an example of R21, it is CH₂=CHCH₂-, CH₂=CHCH₂CH₂-, CH₂=CH-, CH₂=C(CH₃)CH₂-, CH₂=CHC₆H₄-, etc., and is CH₂=CHCH₂- preferably. Moreover, as a desirable range of n21, it is 4 to about 20. Specifically as this polyalkylene oxide compound, there is a compound shown by the formula (2-1-1).

[0026]

[Formula 20]

(2-1-1)



[0027] Thus, the polysiloxane compound of the produced general formula (1-1) and the polyalkylene oxide compound of a general formula (2-1) are heated by the hydrosilylation reaction also as a catalyst, and a polymerization is carried out. A polymerization continues until a reactional phase hand is no longer found out, and the purpose compound (1) of this invention is obtained. If the above-mentioned polysiloxane compound and a polyalkylene oxide compound set an Si-H basis to 1, they will be mixed by the ratio to which an alkenyl machine becomes 0.8 to about 1.2 from 0.5 preferably about two. If the polyalkylene oxide compound is superfluous at this time, an alkenyl machine will remain in both ends, and if the polysiloxane compound is conversely superfluous, an Si-H basis remains in both ends. And it depends on the preparation concentration of a reactant etc. for the average molecular weight of the purpose compound (1) obtained.

[0028] Moreover, if what carried out alkoxy denaturation of the piece end of the polyalkylene oxide section (compound shown by the below-mentioned general formula (2-2)) is added, this serves as the last polymerization edge and can control the average molecular weight by this. Thus, the obtained purpose compound (1) has polysiloxane structure and polyalkylene oxide structure by turns, and the number of repeat structures is 4 to about 80 preferably about 100 from 2. As the manufacture method of the compound which carried out alkoxy denaturation of the piece end of this polyalkylene oxide section, the polymerization of the ***** which has epoxy groups, such as an ethyleneoxide, is carried out to alcohol, such as a methanol, ethanol, and a butanol, by ring opening polymerization, for example, and the polyalkylene oxide which has a hydroxyl group at one end is obtained. Thus, the compound shown by the obtained following general formula (2-2) is a polyalkylene oxide compound with which the hydroxyl group in one end of polyalkylene oxide is replaced by the vinyloxy machine, the aryloxy group, or 2-methyl allyloxy machine, it has an alkenyl machine in one side, and alkoxy denaturation of the piece end was carried out.

[0029]

[Formula 21]

R₂₂-O-(C_bH_{2b}-O)_{n₂₂}-R₂₃

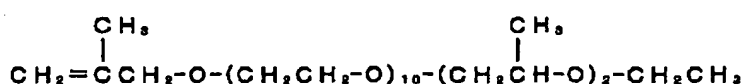
(2-2)

R22 shows among a formula the hydrocarbon group which has an end double bond, R23 shows a hydrogen atom, a monovalent saturated-hydrocarbon machine, or an acyl group, b shows the integer of 2 to 4, and n22 shows one or more integers. In this case, as an example of R22, there are CH₂=CHCH₂-, CH₂=CHCH₂CH₂-, CH₂=CH-, CH₂=C(CH₃)CH₂-, CH₂=CHC₆H₄-, etc., and they are CH₂=CHCH₂- and CH₂=C(CH₃)CH₂- preferably. As a desirable range of n22, it is 4 to about 20. As an example of the monovalent saturated-hydrocarbon machine in R23, the alkyl group of the carbon numbers 1-18, such as a methyl group and an ethyl group, etc. is mentioned. As a desirable example of R23, they are a hydrogen atom, a methyl group, an ethyl group, a butyl, or an acyl group. Specifically as a polyalkylene oxide compound with which alkoxy denaturation of this piece end was carried out, there is a compound shown by the following formula (2-2-1).

[0030]

[Formula 22]

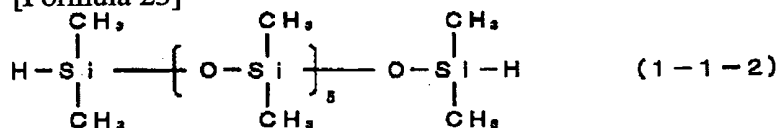
(2-2-1)



[0031] Next, the structure-of-cross-linkage object which mixes the polyalkylene oxide compound of the general formula (2-1) which has an alkylene machine, and the polyfunctional compound (polyfunctional compound shown by the below-mentioned general formula (3-1)) for forming the structure of cross linkage to both ends, and is acquired by the polysiloxane compound of the general formula (1-1) which has an Si-H basis in both ends by the hydrosilylation reaction as another mode of this invention is the purpose compound (2) of this invention. When the compound of a formula (1-1), the compound of a formula (2-1), and the compound of a formula (3-1) set the Si-H basis of the compound of a formula (1-1) to 1 at this time, the alkenyl machine of the compound of a formula (2-1) makes it react by the ratio from which 0.1 to about 1.99 and the alkenyl machine of the compound of a formula (3-1) become 0.01 to about 1.99. When producing the purpose compound (2), as a polysiloxane compound of a formula (1-1), m1 is desirable and zero to 50 or less integer and the thing which is one to 20 or less integer still more preferably are desirable. Specifically as a compound applicable to this, there is a compound shown by the following formula (1-1-2).

[0032]

[Formula 23]



[0033] Although the polyfunctional compound used for producing the purpose compound (2) is shown by the following general formula (3-1), this polyfunctional compound has three or more unsaturation hydrocarbon groups, causes the Si-H basis of the compound of a formula (1-1) or the Si-H basis of the reactant of the compound of a formula (1-1), and the compound of a formula (2-1), and the same hydrosilylation reaction as the above, and forms a structure-of-cross-linkage object.

[0034]

[Formula 24]

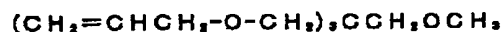


Among a formula, R31 shows alkyl groups, such as a hydrogen atom or a methyl group, and an ethyl group, and is a hydrogen atom or a methyl group preferably. R32 shows a bivalent machine or direct coupling, and has a methylene group, an ethylene, a phenylene group, etc. as an example of a bivalent organic machine. l3 is two or more integers, and is 3 or 4 preferably. Z31 is a substituent containing carbon or nitrogen, and is a basis with the same valence as l3. As a thing applicable to this polyfunctional compound The formula (3-1-1) specifically shown below, a formula (3-1-2), a formula (3-1-3), There is a compound of a formula (3-1-4), a formula (3-1-5), a formula (3-1-6), a formula (3-1-7), a formula (3-1-8), a formula (3-1-9), a formula (3-1-10), a formula (3-1-11), or a formula (3-1-12) etc.

[0035]

[Formula 25]

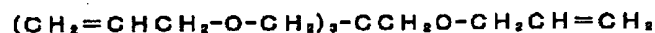
(3-1-1)



[0036]

[Formula 26]

(3-1-2)



[0037]

[Formula 27]

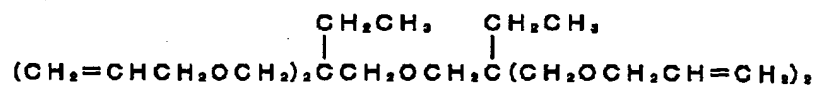
(3-1-3)



[0038]

[Formula 28]

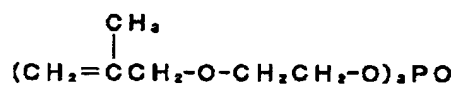
(3-1-4)



[0039]

[Formula 29]

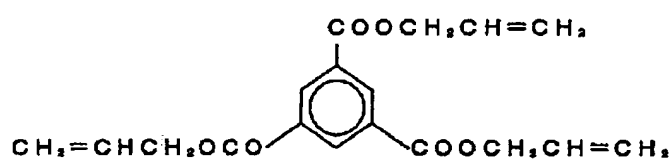
(3-1-5)



[0040]

[Formula 30]

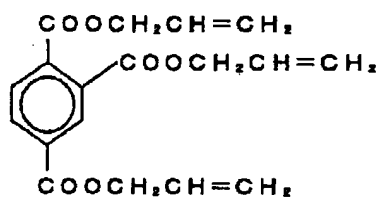
(3-1-6)



[0041]

[Formula 31]

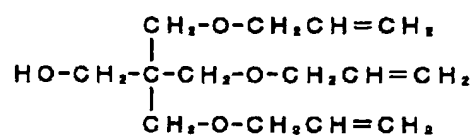
(3-1-7)



[0042]

[Formula 32]

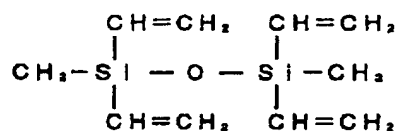
(3-1-8)



[0043]

[Formula 33]

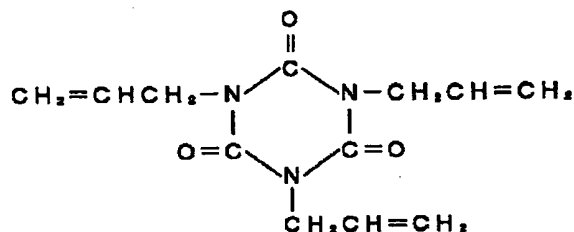
(3-1-9)



[0044]

[Formula 34]

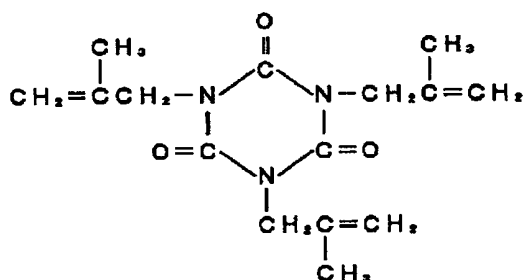
(3-1-10)



[0045]

[Formula 35]

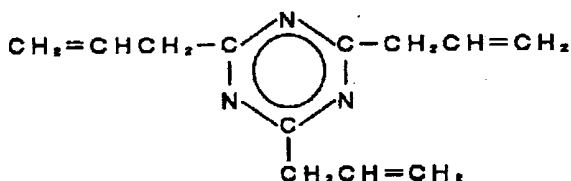
(3-1-11)



[0046]

[Formula 36]

(3-1-12)

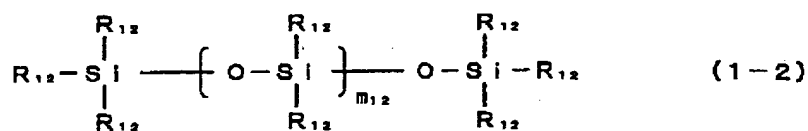


[0047] When obtaining the purpose compound (2), the polyfunctional compound of a general formula (3-1) has further the polysiloxane compound of a general formula (1-1), the polyalkylene oxide compound of a general formula (2-1), and the case where the compatibility between each compound becomes remarkably bad, from the relation of molecular weight etc. In this case, the compound of a general formula (2-1) can be made to be able to react by the hydrosilylation reaction in the superfluous state of the compound of a general formula (1-1) beforehand, a precursor with moderate molecular weight can be produced, the polyfunctional compound of a general formula (3-1) can be made to be able to act on this, and a structure-of-cross-linkage object can also be acquired. Specifically, if the Si-H basis of the compound of a general formula (1-1) is set to 1, make the alkenyl machine of the compound of a general formula (2-1) react by the ratio which becomes 0.1 to about 1.99, and will produce a precursor, the alkenyl machine of the polyfunctional compound of a general formula (3-1) will be made to react further by the ratio which becomes 0.01 to about 1.9, and it will obtain.

[0048] Next, the structure-of-cross-linkage object reacted and acquired as still more nearly another mode of this invention in the polysiloxane which has three or more Si-H bases, the polyalkylene oxide compound of a general formula (2-1) or a formula (2-2), and the polyfunctional compound of a general formula (3-1) is the purpose compound (3) of this invention. There is a straight chain-like polysiloxane shown by the general formula (1-2) shown below as a polysiloxane which has three or more Si-H bases, an annular polysiloxane shown by the general formula (1-3), or a ladder-like polysiloxane shown by the general formula (1-4).

[0049]

[Formula 37]

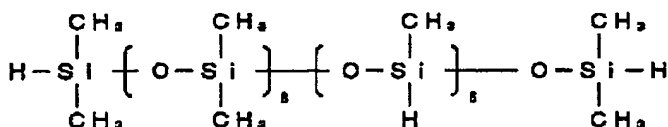


Among a formula, although R21 shows the monovalent hydrocarbon group or monovalent hydrogen atom which does not include an aliphatic unsaturation independently mutually, three [of a molecule] or more of R12 are a hydrogen atom, and 50 or less pieces are 3 to about ten desirable still more preferably. m12 shows the integer of 0 to 500. The desirable range of m12 is 2 to about 100, and is 5 to about 30 still more preferably. In addition, specifically as a compound applicable to this, there is a compound of the following formula (1-2-1).

[0050]

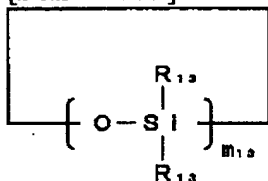
[Formula 38]

(1-2-1)



[0051]

[Formula 39]

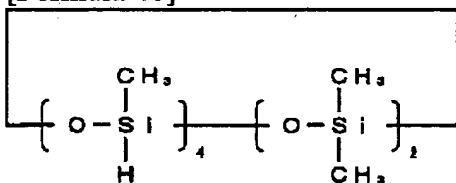


(1-3)

R13 shows among a formula a hydrogen atom or the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually, and three in a molecule to eight of R13 pieces are hydrogen atoms. m13 shows the integer of 3 to 8. In addition, specifically as a compound applicable to this, there is a compound of the following formula (1-3-1).

[0052]

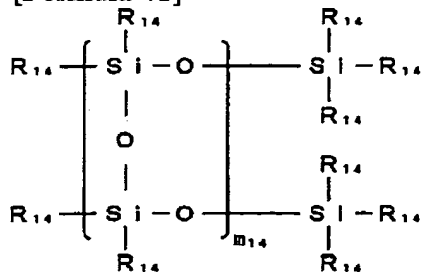
[Formula 40]



(1-3-1)

[0053]

[Formula 41]

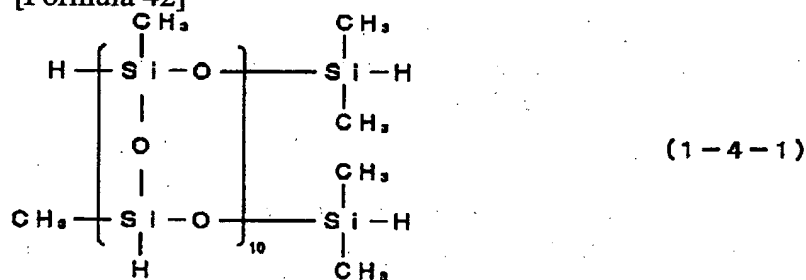


(1-4)

R14 shows among a formula a hydrogen atom or the monovalent hydrocarbon group which does not include an aliphatic unsaturation independently mutually, three [of a molecule] or more of R14 are a hydrogen atom, and they are 50 or less pieces preferably. m14 is the integers from 1 to 50, and is 4 to about 20 still more preferably about 30 from 2 preferably. In addition, specifically as a compound applicable to this, there is a compound of the following formula (1-4-1).

[0054]

[Formula 42]



[0055] If the Si-H basis of the polysiloxane which has such three or more Si-H bases is set to 1, the purpose compound (3) of this invention By the ratio from which the alkenyl machine of the compound of a general formula (2-1) becomes 0.1 to about 0.99, or the ratio from which the alkenyl machine of the compound of a general formula (2-2) becomes 0.1 to about 0.9 Furthermore, it is obtained by making it react by the ratio from which the alkenyl machine of the compound of a general formula (3-1) becomes 0.01 to about 0.8. Moreover, it obtains, and it can continue, a precursor can be made to make the polysiloxane which has three or more Si-H bases beforehand, the compound of a general formula (2-1), and the compound of a general formula (2-1) react by such ratio like the time of obtaining the purpose compound (2) as an option, and to be able to react with the compound of a general formula (3-1), and it can also obtain.

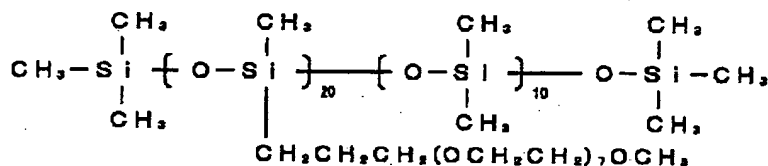
[0056] The purpose compound (1) mentioned above The gel electrolyte containing either and denaturation silicone of - (3) is also one mode of this invention. Denaturation silicone here means polyether denaturation silicone, polyester denaturation silicone, etc. of denaturation silicone, such as alkoxy denaturation silicone, alcoholic denaturation silicone, carboxy denaturation silicone, epoxy denaturation silicone, and amino denaturation silicone, the shape of the shape of a pendant, and a straight chain, piece end denaturation, and both-ends denaturation. Although such viscosity is 10000 or less cPs at 40 degrees C, it is 1000 or less cPs still more preferably 2000 or less cPs preferably. if it sets the purpose compound to 1 as the ratio in mixing either and these denaturation silicone of purpose compound (1) - (3) -- denaturation silicone -- a 0.01 to 100-fold quantitative-ratio grade -- it is preferably mixed and used by 0.1 to 10-fold quantitative-ratio grade

[0057] Especially as denaturation silicone used, polyether denaturation silicone is desirable and denaturalizes in the shape of a pendant more preferably. Specifically as desirable denaturation silicone, what is shown by a following formula (4-1) and a following formula (4-2) is mentioned. When the viscosity of the denaturation silicone of this formula (4-1) was measured by the Brookfield viscometer (the rotor number 2, rotational frequency 60rpm) by Tokyo Keiki Co., Ltd. which is a rotational viscometer, it was 173cP(s) at 40 degrees C.

[0058]

[Formula 43]

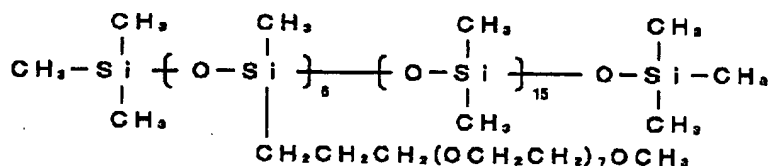
(4-1)



[0059]

[Formula 44]

(4-2)



* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, although an example explains this invention in detail further, unless the main point of this invention is exceeded, it is not limited to these.

[0065] Each material of the primary example was mixed.

The compound of a formula (1-1-1) The compound of a 160 weight sections type (2-1-1) 97 weight sections propylene carbonate 100 weight sections lithium perchlorate 0.3% platinum catalyst of 36 weight sections the 2.5 weight sections -- this -- the amount of eyes of 15g/m² -- a nonwoven fabric with a thickness of 30 micrometers -- sinking in -- 90 degrees C -- 1 hour -- heating . The gel electrolyte (1) with a thickness of 32 micrometers was obtained. The storage modulus of this gel electrolyte (1) was 8.5x10³Pa, and electrical conductivity was 6.5x10⁻⁴ S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (1), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 1.8 mAh/cm².

[0066] Each material of the secondary example was mixed.

The compound of a formula (1-1-2) The 67.3 weight sections The compound of a formula (2-1-1) The 84.1 weight sections The compound of a formula (3-1-1) The 13.7 weight sections Ethylene carbonate 40 weight sections Propylene carbonate 60 weight sections Trifluoromethane sulfonic-acid lithium The 39.8 weight sections 0.3% platinum catalyst the 1.2 weight sections -- this -- amount of eyes 15 g/m² -- a nonwoven fabric with a thickness of 30 micrometers -- sinking in -- 90 degrees C -- 1 hour -- heating . The gel electrolyte (2) with a thickness of 32 micrometers was obtained. The storage modulus of this gel electrolyte (2) was 0.9x10⁵Pa, and electrical conductivity was 8.0x10⁻⁴ S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (2), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 1.8 mAh/cm².

[0067] Each material of the 3rd example was mixed, it heated at 100 degrees C for 30 minutes, and the precursor (3) was produced.

compound of a formula (1-1-2) The 67.3 weight sections Compound of a formula (2-1-1) The 84.1 weight sections 0.3% platinum catalyst the 1.4 weight sections -- next, each following compound was mixed with the above-mentioned precursor (3)

A precursor (3) The 151.4 weight sections The compound of a formula (3-1-1) 13.7 Weight section Ethylene carbonate 40 weight sections Propylene carbonate 60 weight sections trifluoromethane sulfonic-acid lithium The 39.8 weight sections 0.3% platinum catalyst the 1.2 weight sections -- this -- amount of eyes 15 g/m² -- a nonwoven fabric with a thickness of 30 micrometers -- sinking in -- 90 degrees C -- 1 hour -- heating . The gel electrolyte (3) with a thickness of 32 micrometers was obtained. The storage modulus of this gel electrolyte (3) was 1.5x10⁵Pa, and electrical conductivity was 7.5x10⁻⁴ S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (3), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were

performed for this cell by the current value of 0.1mA, the capacity was 1.9 mAh/cm².

[0068] Each material of the 4th example was mixed, it heated at 100 degrees C for 30 minutes, and the precursor (4) was produced.

The compound of a formula (1-2-1) The 43.5 weight sections The compound of a formula (2-1-1) The 50.2 weight sections The compound of a formula (2-2-2) The 72.6 weight sections The compound of a formula (3-1-6) The 21.2 weight sections Ethylene carbonate 50 weight sections Dimethoxyethane 50 weight sections Lithium perchlorate 28 weight sections 0.3% platinum catalyst the 2.5 weight sections -- this -- the amount of eyes of 15g/m² -- a nonwoven fabric with a thickness of 30 micrometers -- sinking in -- 90 degrees C -- 1 hour -- heating . The gel electrolyte (4) with a thickness of 32 micrometers was obtained. The storage modulus of this gel electrolyte (4) was 1.4x10⁵Pa, and electrical conductivity was 6.0x10⁻⁴ S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (4), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 2.0 mAh/cm².

[0069] Each material of the 5th example was mixed.

The compound of a formula (1-1-1) 160 Weight section The compound of a formula (2-1-1) 97 Weight section The compound of a formula (4-1) 100 The weight section Trifluoromethane sulfonic-acid lithium 35 weight sections 0.3% platinum catalyst the 2.5 weight sections -- this -- a flat-surface top -- developing . It heated at 90 degrees C for 1 hour, and the gel electrolyte (5) with a thickness of 40 micrometers was obtained. The storage modulus of this gel electrolyte (5) was 4.5x10⁵Pa, and electrical conductivity was 7.0x10⁻⁴ S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (5), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 1.8 mAh/cm².

[0070] Each material of the 6th example was mixed.

A precursor (3) The 149.6 weight sections The compound of a formula (3-1-6) The 17.4 weight sections The compound of a formula (4-1) 60 weight sections Propylene carbonate 40 weight sections Lithium perchlorate 27 weight sections 0.3% platinum catalyst the 0.8 weight sections -- this -- a flat-surface top -- developing . It heated at 90 degrees C for 1 hour, and the gel electrolyte (6) with a thickness of 40 micrometers was obtained. The storage modulus of this gel electrolyte (6) was 9.5x10⁵Pa, and electrical conductivity was 7.0x10⁻⁴ S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (6), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of 0.1mA, the capacity was 1.7 mAh/cm².

[0071] Each material of the 7th example was mixed.

The compound of a formula (1-2-1) The 43.5 weight sections The compound of a formula (2-1-1) The 50.2 weight sections The compound of a formula (2-2-1) The 72.6 weight sections The compound of a formula (3-1-1) 27 weight sections The compound of a formula (4-1) 60 weight sections Ethylene carbonate 20 weight sections Propylene carbonate 20 weight sections Trifluoromethane sulfonic-acid lithium 44 weight sections 0.3% platinum catalyst the 1.5 weight sections -- this -- a flat-surface top -- developing . It heated at 90 degrees C for 1 hour, and the gel electrolyte (7) with a thickness of 40 micrometers was obtained. The storage modulus of this gel electrolyte (7) was 6.5x10⁵Pa, and electrical conductivity was 5.0x10⁻⁴ S/cm. On the other hand, the positive-electrode layer and the negative-electrode layer were taken out from the commercial lithium rechargeable battery, the laminating of metal aluminum, a positive-electrode layer, a gel electrolyte (7), a negative-electrode layer, and the metal copper was carried out, and the lithium rechargeable battery was produced. When charge and discharge were performed for this cell by the current value of

0.1mA, the capacity was 1.8 mAh/cm².

[0072] The example poly methyl hydrogen siloxane of comparison (average molecular weight 300000) 60 weight section, the polyethylene-glycol monoallyl ether 351 weight section, and the tetrapod ethylene GUREKORU diaryl ether 13.7 weight section were dissolved in the toluene 4000 weight section, the isopropyl alcohol solution (3.8×10^{-3} mol/l.) 80 weight section of a chloroplatinic acid was added as a catalyst, and it heated at 50 degrees C for 48 hours. Next, toluene was removed by reduced pressure drying and the resultant was obtained. In addition to the resultant which produced the tetrahydrofuran solution of a lithium perchlorate 10% of the weight, and produced 40 weight sections previously on the other hand, the tetrahydrofuran was removed for swelling to waiting and the degree, and the electrical conductivity was measured. Consequently, the value of 0.9×10^{-4} S/cm was acquired at the room temperature.

[Translation done.]

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